AFOSR-TR-1238

MF-72

Courant Institute of
Mathematical Sciences

Magneto-Fluid Dynamics Division

Long-Range Correlations in Kinetic Theory

Chelluri C. A. Sastri

Air Force Office of Scientific Research Report
October 1973

New York University

MF-72
c.1

New York University
Courant Institute of Mathematical Sciences
Magneto-Fluid Dynamics Division

MF-72 AFOSR-TR-73-1238

LONG-RANGE CORRELATIONS
IN KINETIC THEORY

Chelluri C. A. Sastri

October 1973

Research sponsored by the Air Force Office of Scientific Research, Air Force Systems Command, USAF under Grant No. AFOSR-71-2053. The United States Government is authorized to reproduce and distribute reprints for governmental purposes not withstanding any copyright notation hereon.

Abstract

It is shown that macroscopic correlations in a fluid are conserved for macroscopically long times. The equations of conservation can be written in a form independent of the density of the fluid and are therefore valid for a liquid as well as a gas. For the purpose of describing correlations in a rarefied gas, a generalization of the Boltzmann equation is suggested which not only gives the correct macroscopic correlation equations but satisfies certain compatibility criteria.

Contents

Section Page

1. Introduction. 1
2. Notation and Conventions. 6
3. Densities 10
4. Some Identities and a Formula of Irving and Kirkwood. 16
5. Conservation Equations of Fluid Dynamics. 20
6. Conservation Equations for Correlations 28
7. Generalization of the Boltzmann Equation. 49
8. Concluding Remarks. 72

References. 73

I. Introduction

The aim of kinetic theory and statistical mechanics is to explain the macroscopic properties of matter on the basis of the properties of the (microscopically small) molecules of which it consists. Accordingly, in kinetic theory, a fluid is regarded as a dynamical system consisting of a very large number of particles — we shall use the terms "molecule" and "particle" synonymously. Two molecules of a fluid are said to be correlated if the position and velocity of one of them are not independent of those of the other.

Correlations are of two kinds — short-range and longe-range. When the distance of separation between any two molecules is of the order of the range of the intermolecular force, the correlation is said to be short-range; when it is considerably larger, the correlation is long-range. Short-range correlations are studied in the theory of dense gases; long-range correlations usually appear in a context apparently unrelated to their microscopic nature, namely, in turbulent fluid dynamics. One of our aims is to clarify this connection.

Contributions to the long-range correlation between any two molecules come from their initial correlation, their present interaction with other molecules, and any collisions that may have taken place between them and other molecules in the past. The Boltzmann equation (see Sec. 7 or Ref. [1] for a derivation), which describes a rarefied gas, is based on the assumption that long-range correlations are negligible. (It is even stated sometimes that, over macroscopic times, they are destroyed by collisions [2].) The question naturally arises whether this assumption is correct. It was conjectured by Grad [3] that it may not always be, and we verify this conjecture. More precisely, his conjecture is that long-range correlations are conserved in the sense that when they are expressed as macroscopic correlations, i.e., as correlations between any two conserved quantities, they obey conservation equations. Thus, if the macroscopic correlations are large initially, they will continue to be large for macroscopically long times.*

Long-range microscopic correlations can be transformed into correlations between macroscopic quantities as follows. By introducing a probability density on the phase space of the system and by localizing, with respect to the molecules, the macroscopic quantities of interest to us — such as mass, momentum and energy, we can calculate their densities in ordinary 3-space. Similarly, given two points in 3-space, we can find the joint density at these points of any two (not necessarily distinct) macroscopic quantities. Subtracting from this joint density the product of the densities of the two quantities at the given points, we get the correlation between them. Our result is that, if each of the two macroscopic quantities is conserved, and if the distance between the two points chosen is larger than a few times the range of the intermolecular force, then the correlation is conserved. In other words, certain moments of long-range correlations are conserved.

---

*Correlations, which we shall study here, refer to one time and two or more positions, whereas fluctuations, which we shall not study here, refer to two or more times and any number of positions. Fluctuations, like correlations, can be studied either from the point of view of fluid dynamics [4] or from that of kinetic theory [5].

The macroscopic correlation equations for a rarefied gas have been given by Zhigulev [6] and Tsugé [7,8]. Tsugé also raised the question of the validity of the Boltzmann equation in the presence of turbulence. It is clear that the equation is valid as long as macroscopic correlations are small, i.e., as long as the motion of the fluid is not turbulent. When there is turbulence, all the derivations of the equation break down, but it is not clear whether the equation itself remains valid. At any rate, in order to obtain the correct macroscopic correlation equations for a rarefied gas, one should replace the Boltzmann equation by a kinetic equation or sequence of equations which includes correlations. This is precisely what we do in Section 7. Our work could thus be interpreted as a further step toward a kinetic theory of turbulence along the lines of Zhigulev and Tsugé.*

A few remarks are now in order. Conventional thermodynamics is based on the assumption that the system has only two time-independent integrals, namely, mass and energy. If the system has other integrals, the thermodynamics that ensues differs from conventional thermodynamics and has been discussed by Grad [10,11] and Lewis [12]. Fluid dynamics, however, is based on the existence of another integral, namely, momentum. Systems whose angular momentum is conserved are also sometimes considered[10,11,13,14]. For the sake of generality, we consider a system whose molecules have internal degrees of freedom and which has any or all of the above types of integrals. Also, our derivation is valid even when the intermolecular forces are velocity dependent, though we require that the divergence with respect to velocity of the force vanish.

---

*The idea that microscopic correlation functions can be used to describe turbulence occurs in Ref. [9], but no equations for macroscopic correlations are derived.

The method we use is essentially the same as that developed by Grad [11] in his generalization of Irving and Kirkwood's [15] derivation of the conservation equations of fluid dynamics. Grad's method is more general than that of Irving and Kirkwood in two ways: (1) Instead of considering only mass, momentum, and energy as Irving and Kirkwood did, he considered general integrals which are purely additive — as mass and momentum are — or which have a purely additive part and a part that consists of two-body interactions, as energy does. (2) He considered systems which have internal degrees of freedom.

Because of the generality, Grad's method is readily applicable to our problem. Essentially, it consists in computing the density, in 3-space, of an arbitrary integral, multiplying the Liouville equation by it, and integrating the resulting equation with respect to everything except the space coordinate. What one gets then is an equation for the rate of change of the density of the integral. In order to show that it is a conservation equation, one has to just show that the terms other than the convective derivative of the density are divergences of some vector functions. To derive the conservation equations for macroscopic correlations, we proceed in a similar manner. We first compute the joint density in 3-space of a pair of integrals, then by multiplying the Liouville equation by it and integrating with respect to everything except the two space coordinates involved, obtain an equation for the rate of change of the density. It turns out that, if the two space coordinates are separated by a sufficiently large distance, the rate equation becomes a conservation equation. Using this equation and the equations for the conservation of the density of each of the two integrals, we get the conservation equation for the correlation between them.

We assume that the molecules of the fluid obey the laws of classical mechanics. Also, for the sake of completeness of presentation, we will reproduce the relevant portions of Grad's paper. In particular, the material of Sections 4 and 5 is taken from his paper.

I take this opportunity to express my sincere gratitude to my teacher Prof. Harold Grad, who not only suggested the problem but provided constant encouragement and guidance. Also, I thank Miss Rachelle Rousso for her painstaking typing of the manuscript.

2. Notation and Conventions

We consider a system consisting of N particles, each of which has s degrees of freedom — 3 external and s-3 internal. We denote the coordinates of the i-th molecule by

$$P_i = (x_i, \xi_i, q_i, p_i)$$

where x_i is the position vector of the center of mass of the molecule and $\xi_i = \frac{dx_i}{dt}$ is the velocity vector of the center of mass. The q_i denote internal coordinates and the $p_i = \frac{dq_i}{dt}$ denote internal velocities.

Let

$$P = (P_1, P_2, P_3, \ldots, P_N)$$

denote a point in the 2Ns-dimensional phase space of the system. We introduce a probability density $f(P,t)$ on this space and normalize it:

$$\int f(P,t)\,dP = 1 ,$$

where the integration extends over the entire phase space. Whenever we suppress the time coordinate - as we did above - we mean that all the quantities appearing are considered at one instant of time, viz., t. Now, we consider a one-phase, one-component system, so that all the molecules are identical. So we assume that f is symmetric in all the particles, and define the reduced or marginal densities - called the one-particle distribution function, the two-particle distribution function, etc. - by

$$f_1(P_1) = \int f \, dP_2 dP_3 \ldots dP_N ,$$

$$f_{12}(P_1, P_2) = \int f \, dP_3 dP_4 \ldots dP_N ,$$

and so on. Since we will need only the first four or five distribution functions, we adopt the convention that if r is the total number of subscripts of a distribution function, then it is the r-particle distribution function; the subscripts themselves indicate the arguments of the function. For instance, f_{245} is the three-particle distribution function of the particles labeled 2, 4, and 5. Clearly, the reduced densities are symmetric and normalized to 1.

The density f changes in time but in such a way that it satisfies the Liouville equation:

$$\frac{\partial f}{\partial t} + \sum_{i=1}^{N} \left(\frac{\partial f}{\partial x_i} \cdot \xi_i + \frac{\partial f}{\partial \xi_i} \cdot F_i + \frac{\partial f}{\partial q_i} \cdot p_i + \frac{\partial f}{\partial p_i} \cdot G_i \right) = 0 , \qquad (2\text{-}1)$$

where $F_i = \frac{d\xi_i}{dt}$ is the acceleration of the center of mass, and $G_i = \frac{dp_i}{dt}$ is the internal acceleration of the i-th molecule. Here, the • refers to summation over the three external, or the s-3 internal, degrees of freedom.

We write

$$F_i = \sum_{j=1}^{N} F_{ij} , \qquad G_i = \sum_{j=1}^{N} G_{ij} , \qquad (2\text{-}2)$$

where F_{ij} is the acceleration of the center of mass of the i-th molecule due to the j-th molecule; similarly for G_{ij}. F_{ii} and G_{ii} are the accelerations of the i-th particle due to external forces. We assume that

$$F_{ii} = F_{11}(P_i), \quad G_{ii} = G_{11}(P_i) \tag{2-3}$$

and

$$F_{ij} = F_{12}(P_i, P_j), \quad G_{ij} = G_{12}(P_i, P_j) \ .$$

We consider two cases; an integral ε can be of type (a):

$$\varepsilon = \sum_{i=1}^{N} \varepsilon_i \ , \quad \varepsilon_i = \varepsilon_1(P_i)$$

or type (b):

$$\varepsilon = \sum_{i=1}^{N} \varepsilon_i + \sum_{\substack{i,j=1 \\ i<j}}^{N} \varepsilon_{ij} \ , \quad \varepsilon_i = \varepsilon_1(P_i), \text{ and } \varepsilon_{ij} = \varepsilon_{12}(P_i, P_j)$$

We assume that $\varepsilon_{ij} = \varepsilon_{ji}$. If ψ is any phase function, i.e., if $\psi = \psi(P_1, P_2, \ldots, P_N)$, we define two mean values:

$$\overline{\psi}(x_1) = N \int \psi f \, \frac{dP_1 dP_2 \ldots dP_N}{dx_1}$$

and

$$\overline{\psi}(x_1, x_2) = N(N-1) \int \psi f \, \frac{dP_1 dP_2 \ldots dP_N}{dx_1 dx_2} \ .$$

Here, the convention is that the integration is performed with respect to all the variables except those appearing in the denominator. The expected value $\langle \psi \rangle$ of ψ is defined by

$$\langle \psi \rangle = \int \psi f dP .$$

3. Densities

In order to calculate the amount of ε in any region D, we have to localize it. This we do as follows: ε_i is localized at x_i, the center of the molecule, and ε_{ij} is localized half at x_i and half at x_j.

Let D_1, D_2 be any regions in 3-space and let ϕ_1, ϕ_2 denote their characteristic functions respectively. The number ν_{D_1} of molecules whose centers lie in D_1 is given by $\nu_{D_1} = \sum_{i=1}^{N} \phi_1(x_i)$. Its expected value is

$$\langle \nu_{D_1} \rangle = \sum_{i=1}^{N} \int f\phi_1(x_i)\,dP = N \int_{x_1 \varepsilon D_1} f_1(P_1)\,dP_1 \ .$$

Hence, the number density ν in 3-space is $N \int f_1 \frac{dP_1}{dx_1}$. The number of pairs of molecules such that one is in D_1 and the other is in D_2 is

$$\sum_{i,j} \phi_1(x_i)\phi_2(x_j) = \sum_{i} \phi_1(x_i)\phi_2(x_i) + \sum_{i \neq j} \phi_1(x_i)\phi_2(x_j) \ .$$

The first sum on the right hand side takes into account the situation where one particle is in $D_1 \cap D_2$ and is counted as a (spurious) pair. By calculating the expected number of pairs, we find that the pair density is given by

$$N\delta(x_1 - x_2) \int f_1 \frac{dP_1}{dx_1} + N(N-1) \int f_{12} \frac{dP_1 dP_2}{dx_1 dx_2} \ .$$

To calculate the density of an integral ε, suppose first that it is of type (a). Then the amount ε_{D_1} of ε in D_1 is $\sum_{i} \phi_1(x_i)\varepsilon_i$, and

$$\langle \varepsilon_{D_1} \rangle = \sum_i \int \phi_1(x_i)\,\varepsilon_i f dP$$

$$= N \int_{x_1 \varepsilon D_1} f_1 \varepsilon_1 dP_1 \ .$$

Hence, the density of ε is

$$N \int \varepsilon_1 f_1 \frac{dP_1}{dx_1} \tag{3-1}$$

If ε is of type (b),

$$\varepsilon_{D_1} = \sum_i \phi_1(x_i)\,\varepsilon_i + \frac{1}{2} \sum_{i \neq j} \phi_1(x_i)\,\varepsilon_{ij} \ .$$

$$\langle \varepsilon_{D_1} \rangle = \sum_i \int \phi_1(x_i)\,\varepsilon_i f dP + \frac{1}{2} \sum_{i \neq j} \int \phi_1(x_i)\,\varepsilon_{ij} f dP$$

$$= N \int_{x_1 \varepsilon D_1} \varepsilon_1 f_1 dP_1 + \frac{N(N-1)}{2} \int_{x_1 \varepsilon D_1} \varepsilon_{12} f_{12} dP_1 dP_2 \ .$$

So, the density of ε is

$$N \int \varepsilon_1 f_1 \frac{dP_1}{dx_1} + \frac{N(N-1)}{2} \int \varepsilon_{12} f_{12} \frac{dP_1 dP_2}{dx_1} \tag{3-2}$$

Now, we shall calculate the joint density of any pair of integrals. There are three cases:

(1) Both integrals are of type (a).

(2) One integral is of type (a), and the other, of type (b).

(3) Both integrals are of type (b).

Strictly speaking, case (3) subsumes cases (1) and (2). Nevertheless, for the sake of convenience and clarity, we shall do them separately.

Case (1): ε', ε'' both of type (a).

$$\varepsilon'_{D_1} = \sum_i \phi_1(x_i)\varepsilon'_i \, ,$$

$$\varepsilon''_{D_2} = \sum_j \phi_2(x_j)\varepsilon''_j \, .$$

$$\langle \varepsilon'_{D_1}\varepsilon''_{D_2} \rangle = \sum_i \int \phi_1(x_i)\phi_2(x_i)\varepsilon'_i\varepsilon''_i f dP + \sum_{i \neq j} \int \phi_1(x_i)\phi_2(x_j)\varepsilon'_i\varepsilon''_j f dP$$

$$= N \int_{x_1 \varepsilon D_1 \cap D_2} \varepsilon'_1\varepsilon''_1 f_1 dP_1 + N(N-1) \int_{\substack{x_1 \varepsilon D_1 \\ x_2 \varepsilon D_2}} \varepsilon'_1\varepsilon''_2 f_{12} dP_1 dP_2 \, .$$

So, the joint density of ε' and ε'' is

$$N\delta(x_1 - x_2) \int \varepsilon'_1\varepsilon''_1 f_1 \frac{dP_1}{dx_1} + N(N-1) \int \varepsilon'_1\varepsilon''_2 f_{12} \frac{dP_1 dP_2}{dx_1 dx_2} \, . \qquad (3\text{-}3)$$

Case (2): ε' of type (a) and ε'' of type (b).

$$\varepsilon'_{D_1} = \sum_i \phi_1(x_i)\varepsilon_i \, ,$$

$$\varepsilon''_{D_2} = \sum_j \phi_2(x_j)\varepsilon''_j + \frac{1}{2} \sum_{j \neq k} \varepsilon''_{jk}\phi_2(x_j) \, .$$

$$\langle \varepsilon'_{D_1}\varepsilon''_{D_2} \rangle = \sum_i \int \varepsilon'_i\varepsilon''_i\phi_1(x_i)\phi_2(x_i) f dP + \sum_{i \neq j} \int \varepsilon'_i\varepsilon''_j\phi_1(x_i)\phi_2(x_j) f dP$$

$$+ \frac{1}{2} \sum_{i \neq k} \int \varepsilon'_i\varepsilon''_{ik}\phi_1(x_i)\phi_2(x_i) f dP + \frac{1}{2} \sum_{i \neq j} \int \varepsilon'_i\varepsilon''_{ij}\phi_1(x_i)\phi_2(x_j) f dP$$

$$+ \frac{1}{2} \sum_{i \neq j \neq k} \int \varepsilon'_i\varepsilon''_{jk}\phi_1(x_i)\phi_2(x_j) f dP$$

$$= N \int_{x_1 \varepsilon D_1 \cap D_2} \varepsilon'_1\varepsilon''_1 f_1 dP_1 + N(N-1) \int_{\substack{x_1 \varepsilon D_1 \\ x_2 \varepsilon D_2}} \varepsilon'_1\varepsilon''_2 f_{12} dP_1 dP_2$$

$$+ \frac{N(N-1)}{2}\int\limits_{x_1 \varepsilon D_1 \cap D_2} \varepsilon_1' \varepsilon_{12}'' f_{12} dP_1 dP_2 + \frac{N(N-1)}{2}\int\limits_{\substack{x_1 \varepsilon D_1 \\ x_2 \varepsilon D_2}} \varepsilon_1' \varepsilon_{12}'' f_{12} dP_1 dP_2$$

$$+ \frac{N(N-1)(N-2)}{2}\int\limits_{\substack{x_1 \varepsilon D_1 \\ x_2 \varepsilon D_2}} \varepsilon_1' \varepsilon_{23}'' f_{123} dP_1 dP_2 dP_3$$

Hence, the joint density of ε' and ε'' is

$$\begin{aligned} & N\delta(x_1-x_2)\int \varepsilon_1'\varepsilon_1'' f_1 \frac{dP_1}{dx_1} + N(N-1)\int \varepsilon_1'\varepsilon_2'' f_{12} \frac{dP_1 dP_2}{dx_1 dx_2} \\ & + \frac{N(N-1)}{2}\,\delta(x_1-x_2)\int \varepsilon_1'\varepsilon_{12}'' f_{12} \frac{dP_1 dP_2}{dx_1} + \frac{N(N-1)}{2}\int \varepsilon_1'\varepsilon_{12}'' f_{12} \frac{dP_1 dP_2}{dx_1 dx_2} \qquad (3\text{-}4) \\ & + \frac{N(N-1)(N-2)}{2}\int \varepsilon_1'\varepsilon_{23}'' f_{123} \frac{dP_1 dP_2 dP_3}{dx_1 dx_2} \;. \end{aligned}$$

Case (3): ε', ε'' both of type (b).

Proceeding as in cases (1) and (2), we find that the joint density of ε' and ε'' is

$$\begin{aligned} & N\delta(x_1-x_2)\int \varepsilon_1'\varepsilon_1'' f_1 \frac{dP_1}{dx_1} + N(N-1)\int \varepsilon_1'\varepsilon_2'' f_{12} \frac{dP_1 dP_2}{dx_1 dx_2} \\ & + \frac{N(N-1)}{2}\delta(x_1-x_2)\int \varepsilon_1'\varepsilon_{12}'' f_{12} \frac{dP_1 dP_2}{dx_1} + \frac{N(N-1)}{2}\int \varepsilon_1'\varepsilon_{12}'' f_{12} \frac{dP_1 dP_2}{dx_1 dx_2} \\ & + \frac{N(N-1)(N-2)}{2}\int \varepsilon_1'\varepsilon_{23}'' f_{123} \frac{dP_1 dP_2 dP_3}{dx_1 dx_2} + \frac{N(N-1)}{2}\delta(x_1-x_2)\int \varepsilon_{12}'\varepsilon_1'' f_{12} \frac{dP_1 dP_2}{dx_1} \\ & + \frac{N(N-1)}{2}\int \varepsilon_{12}'\varepsilon_2'' f_{12} \frac{dP_1 dP_2}{dx_1 dx_2} + \frac{N(N-1)(N-2)}{2}\int \varepsilon_{13}'\varepsilon_2'' f_{123} \frac{dP_1 dP_2 dP_3}{dx_1 dx_2} \\ & + \frac{N(N-1)}{4}\delta(x_1-x_2)\int \varepsilon_{12}'\varepsilon_{12}'' f_{12} \frac{dP_1 dP_2}{dx_1} \end{aligned}$$

$$+ \frac{N(N-1)(N-2)}{4} \delta(x_1 - x_2) \int \varepsilon'_{12} \varepsilon''_{13} f_{123} \frac{dP_1 dP_2 dP_3}{dx_1}$$

$$+ \frac{N(N-1)}{4} \int \varepsilon'_{12} \varepsilon''_{12} f_{12} \frac{dP_1 dP_2}{dx_1 dx_2} + \frac{N(N-1)(N-2)}{4} \int \varepsilon'_{13} \varepsilon''_{21} f_{123} \frac{dP_1 dP_2 dP_3}{dx_1 dx_2}$$

$$+ \frac{N(N-1)(N-2)}{4} \int \varepsilon'_{12} \varepsilon''_{23} f_{123} \frac{dP_1 dP_2 dP_3}{dx_1 dx_2}$$

$$+ \frac{N(N-1)(N-2)}{4} \int \varepsilon'_{13} \varepsilon''_{23} f_{123} \frac{dP_1 dP_2 dP_3}{dx_1 dx_2}$$

$$+ \frac{N(N-1)(N-2)(N-3)}{4} \int \varepsilon'_{13} \varepsilon''_{24} f_{1234} \frac{dP_1 dP_2 dP_3 dP_4}{dx_1 dx_2} \tag{3-5}$$

The joint densities consist of three parts. The terms containing the δ-function give rise to self-fluctuations or auto-correlations. Those in which the molecules at x_1 and x_2 interact with each other either directly or via a third molecule express short-range correlations. The rest of the terms refer to long-range correlations. Since we are interested only in long-range correlations, we assume that the molecules labeled 1 and 2 are far apart. More specifically, if σ denotes the range of the inter-molecular force, we assume that in case (1), particles 1 and 2 are separated by a distance larger than σ. Then the density (3-3) becomes

$$N(N-1) \int \varepsilon'_1 \varepsilon''_2 f_{12} \frac{dP_1 dP_2}{dx_1 dx_2} \tag{3-6}$$

Similarly, if we assume that particles 1 and 2 are separated by a distance greater than 2σ in case (2) and 3σ in case (3), the densities (3-4) and (3-5) become

$$N(N-1)\int \varepsilon_1' \varepsilon_2'' f_{12} \frac{dP_1 dP_2}{dx_1 dx_2} + \frac{N(N-1)(N-2)}{2} \int \varepsilon_1' \varepsilon_{23}'' f_{123} \frac{dP_1 dP_2 dP_3}{dx_1 dx_2} \qquad (3\text{-}7)$$

and

$$N(N-1)\int \varepsilon_1' \varepsilon_2'' f_{12} \frac{dP_1 dP_2}{dx_1 dx_2} + \frac{N(N-1)(N-2)}{2} \int (\varepsilon_1' \varepsilon_{23}'' + \varepsilon_2'' \varepsilon_{13}') f_{123} \frac{dP_1 dP_2 dP_3}{dx_1 dx_2}$$

$$+ \frac{N(N-1)(N-2)(N-3)}{4} \int \varepsilon_{13}' \varepsilon_{24}'' f_{1234} \frac{dP_1 dP_2 dP_3 dP_4}{dx_1 dx_2} \qquad (3\text{-}8)$$

respectively.

4. Some Identities and a Formula of Irving and Kirkwood

We shall now use the fact that ε is an integral. First, we introduce some notation:

$$(i,j) = \frac{\partial \varepsilon_i}{\partial \xi_i} \cdot F_{ij} + \frac{\partial \varepsilon_i}{\partial p_i} \cdot G_{ij} ,$$

and

$$(i,j,k) = \frac{\partial \varepsilon_{ij}}{\partial \xi_i} \cdot F_{ik} + \frac{\partial \varepsilon_{ij}}{\partial p_i} \cdot G_{ik} ;$$

there is no summation on repeated indices.

If there are no external forces acting on a system, we say it is isolated. Suppose that the system is isolated and consists of only one particle. Then

$$\frac{d\varepsilon_1}{dt} = \frac{\partial \varepsilon_1}{\partial x_1} \cdot \xi_1 + \frac{\partial \varepsilon_1}{\partial \xi_1} \cdot F_1 + \frac{\partial \varepsilon_1}{\partial q_1} \cdot p_1 + \frac{\partial \varepsilon_1}{\partial p_1} \cdot G_1 = 0$$

or

$$\frac{\partial \varepsilon_1}{\partial x_1} \cdot \xi_1 + \frac{\partial \varepsilon_1}{\partial q_1} \cdot p_1 = 0 \qquad (4\text{-}1)$$

This is an identity that limits the class of functions ε_1 which make ε an integral. If the system consists of two particles and is isolated, then

$$\frac{d}{dt}(\varepsilon_1 + \varepsilon_2) = 0 \qquad \text{in case (a)}$$

and

$$\frac{d}{dt}(\varepsilon_1 + \varepsilon_2 + \varepsilon_{12}) = 0 \quad \text{in case (b).}$$

Using the identity (4-1), we get

$$(1,2) + (2,1) = 0 \tag{4-2}$$

in case (a), and

$$(1,2) + (2,1) + (1,2,2) + (2,1,1) + \frac{\partial \varepsilon_{12}}{\partial x_1} \cdot \xi_1 + \frac{\partial \varepsilon_{12}}{\partial x_2} \cdot \xi_2 + \frac{\partial \varepsilon_{12}}{\partial q_1} \cdot p_1 + \frac{\partial \varepsilon_{12}}{\partial q_2} \cdot p_2 = 0 \tag{4-3}$$

in case (b).

Now suppose that the system consists of three particles and is isolated. Consider case (b). Then

$$\frac{d}{dt}(\varepsilon_1 + \varepsilon_2 + \varepsilon_3 + \varepsilon_{12} + \varepsilon_{13} + \varepsilon_{23}) = 0$$

Using the identities (4-1) and (4-3), we obtain from this the identity

$$(1,2,3) + (2,1,3) + (2,3,1) + (3,2,1) + (3,1,2) + (1,3,2) = 0 \tag{4-4}$$

We remark that no new identities are obtained by considering systems consisting of more than three particles. Actually, we get no new information even when we consider a system of three particles if we are in case (a), or if we are in case (b) and assume that the intermolecular forces are central.

One can verify the following formula of Irving and Kirkwood [15] by direct differentiation:

If $\vec{x}_1$, $\vec{x}_2$ are vectors and $\vec{K}$ is a vector function defined by

$$\vec{K}(\vec{x}_1) = \frac{1}{2}\int \vec{x}_2 \int_0^1 \phi(\vec{x}_1 - \alpha\vec{x}_2,\ \vec{x}_1 + (1-\alpha)\vec{x}_2)\, d\alpha\, dx_2\ , \tag{4-5}$$

where ϕ is some smooth function and where the x_2-integration extends over the whole space, then

$$\text{div}\ \vec{K} = \frac{\partial}{\partial x_1}\cdot\vec{K} = \frac{1}{2}\int[\phi(\vec{x}_1,\vec{x}_2) - \phi(\vec{x}_2,\vec{x}_1)]dx_2 \tag{4-6}$$

Conversely, the right hand side of (4-6) is the divergence of K (as defined by (4-5)) plus an arbitrary vector function whose divergence vanishes.

We shall make repeated use of this formula to identity certain terms as divergences and the corresponding flow vectors with vectors of the form (4-5). To verify that the latter identification is reasonable, we have to calculate the flow of ε across the surface of a domain D. In order to do this, it is necessary to localize the flow of ε. For the part of ε which is carried by the molecules, this has already been done by the localization of ε. For the part due to intermolecular forces, it is natural in case (a) to localize the flow between two molecules along their line of centers; in case (b), it is not so natural (since the force of molecule 1 on molecule 2 can transfer ε to molecule 3), but justification can be given (see Ref. [11]), and it is assumed. Without actually carrying out the computation (see [15] for an example), we state the result that the flow vector differs from a vector of the form (4-5) by one which is small and localized and whose divergence vanishes.

5. Conservation Equations of Fluid Dynamics

If we multiply (2-1) by $N\varepsilon_1$ and integrate with respect to $\frac{dP}{dx_1}$, we get

$$\frac{\partial\bar{\bar{\varepsilon}}_1}{\partial t} + \frac{\partial}{\partial x_1}\cdot(\overline{\overline{\xi_1\varepsilon_1}}) - (\overline{\overline{\xi_1\cdot\frac{\partial\varepsilon_1}{\partial x_1}}} + \overline{\overline{p_1\cdot\frac{\partial\varepsilon_1}{\partial q_1}}} + \overline{\overline{F_{11}\cdot\frac{\partial\varepsilon_1}{\partial\xi_1}}} + \overline{\overline{G_{11}\cdot\frac{\partial\varepsilon_1}{\partial p_1}}})$$

$$- (N-1)(\overline{\overline{F_{12}\cdot\frac{\partial\varepsilon_1}{\partial\xi_1}}} + \overline{\overline{G_{12}\cdot\frac{\partial\varepsilon_1}{\partial p_1}}}) = 0 , \qquad (5\text{-}1)$$

where we have assumed that f vanishes (or is periodic) at the limits of integration of all the variables.

Similarly, if we multiply (2-1) by $N\varepsilon_{12}$ and integrate with respect to $\frac{dP}{dx_1}$, we get

$$\frac{\partial\bar{\bar{\varepsilon}}_{12}}{\partial t} + \frac{\partial}{\partial x_1}\cdot(\overline{\overline{\xi_1\varepsilon_{12}}}) - [\overline{\overline{\xi_1\cdot\frac{\partial\varepsilon_{12}}{\partial x_1}}} + \overline{\overline{p_1\cdot\frac{\partial\varepsilon_{12}}{\partial q_1}}} + \overline{\overline{\xi_2\cdot\frac{\partial\varepsilon_{12}}{\partial x_2}}} + \overline{\overline{p_2\cdot\frac{\partial\varepsilon_{12}}{\partial q_2}}}$$

$$+ \overline{\overline{(F_{11}+F_{12})\cdot\frac{\partial\varepsilon_{12}}{\partial\xi_1}}} + \overline{\overline{(G_{11}+G_{12})\cdot\frac{\partial\varepsilon_{12}}{\partial p_1}}} + \overline{\overline{(F_{22}+F_{21})\cdot\frac{\partial\varepsilon_2}{\partial\xi_2}}}$$

$$+ \overline{\overline{(G_{22}+G_{21})\cdot\frac{\partial\varepsilon_2}{\partial p_2}}}] - (N-2)[\overline{\overline{F_{13}\cdot\frac{\partial\varepsilon_{12}}{\partial\xi_1}}} + \overline{\overline{G_{13}\cdot\frac{\partial\varepsilon_{12}}{\partial p_1}}} + \overline{\overline{F_{23}\cdot\frac{\partial\varepsilon_{12}}{\partial\xi_2}}}$$

$$+ \overline{\overline{G_{23}\cdot\frac{\partial\varepsilon_2}{\partial p_2}}}] = 0 \qquad (5\text{-}2)$$

Note that the density e of ε in 3-space is given by

$$e = \bar{\bar{\varepsilon}}_1 \qquad \text{in case (a)}$$

and

$$e = \bar{\bar{\varepsilon}}_1 + \frac{(N-1)}{2}\bar{\bar{\varepsilon}}_{12} \qquad \text{in case (b).}$$

Also let

$$\rho_1 = mN \int f_1 \frac{dP_1}{dx_1} ,$$

and let u_1 be defined by

$$\rho_1 u_1 = mN \int \xi_1 f_1 \frac{dP_1}{dx_1} .$$

Let

$$c_1 = \xi_1 - u_1 .$$

u_1 is the macroscopic velocity of the fluid; c_1 is called the peculiar velocity of particle 1.

Next we show that, in the absence of external forces, e obeys an equation of the form

$$\frac{\partial e}{\partial t} + \frac{\partial}{\partial x_1} \cdot (eu_1) + \frac{\partial}{\partial x_1} \cdot Q = 0 , \tag{5-3}$$

where Q is some vector (called the flow vector).

Case (a): If the system is isolated and if we use (4-1), equation (5-1) becomes

$$\frac{\partial e}{\partial t} + \frac{\partial}{\partial x_1} \cdot (eu_1) + \frac{\partial}{\partial x_1} \circ (\overline{\overline{c_1 \varepsilon_1}}) - (N-1)(\overline{\overline{1,2}}) = 0 \tag{5-4}$$

But (4-2) gives

$$(1,2) = \tfrac{1}{2}[(1,2) - (2,1)] .$$

Hence

$$\frac{\partial e}{\partial t} + \frac{\partial}{\partial x_1} \cdot (eu_1) + \frac{\partial}{\partial x_1} \cdot (\overline{\overline{c_1 \varepsilon_1}}) - \frac{(N-1)}{2}[(\overline{\overline{1,2}}) - (\overline{\overline{2,1}})] = 0 \qquad (5\text{-}5)$$

By (4-6), this is in the form (5-3), with

$$Q_a = \overline{\overline{c_1 \varepsilon_1}} - N(N-1)K_a \, , \qquad (5\text{-}6)$$

where K_a is given by (4-5) in terms of

$$\phi_a = \int \left(\frac{\partial \varepsilon_1}{\partial \xi_1} \cdot F_{12} + \frac{\partial \varepsilon_1}{\partial p_1} \cdot G_{12} \right) f_{12} \, \frac{dP_1 dP_2}{dx_1 dx_2} \, .$$

Case (b): Let

$$\overset{*}{\varepsilon}_{12} = \varepsilon_1 + \frac{(N-1)}{2} \varepsilon_{12}$$

Then

$$e = \overline{\overline{\overset{*}{\varepsilon}_{12}}}$$

Again, we assume that the system is isolated. Multiplying (5-2) by $\frac{(N-1)}{2}$ and adding it to (5-4), we get

$$\frac{\partial e}{\partial t} + \frac{\partial}{\partial x_1} \cdot (eu_1) + \frac{\partial}{\partial x_1} \cdot (\overline{\overline{c_1 \overset{*}{\varepsilon}_{12}}}) - (N-1)(\overline{\overline{1,2}}) - \frac{(N-1)(N-2)}{2}[(\overline{\overline{1,2,3}}) + (\overline{\overline{2,1,3}})$$

$$- \frac{(N-1)}{2}\left(\overline{\overline{\frac{\partial \varepsilon_{12}}{\partial x_1} \cdot \xi_1}} + \overline{\overline{\frac{\partial \varepsilon_{12}}{\partial x_2} \cdot \xi_2}} + \overline{\overline{\frac{\partial \varepsilon_{12}}{\partial q_1} \cdot p_1}} + \overline{\overline{\frac{\partial \varepsilon_{12}}{\partial q_2} \cdot p_2}}\right) - \frac{(N-1)}{2}[(\overline{\overline{1,2,2}}) + (\overline{\overline{2,1,1}})$$

$$= 0 \, . \qquad (5\text{-}7)$$

Now, eq. (4-4), together with the symmetry of f, gives

$$(\overline{\overline{1,2,3}}) + (\overline{\overline{2,1,3}}) = \tfrac{1}{3}[(\overline{\overline{1,2,3}}) + (\overline{\overline{2,1,3}}) - (\overline{\overline{2,3,1}}) - (\overline{\overline{3,2,1}})]$$

$$= \tfrac{1}{3}[(\overline{\overline{1,3,2}}) + (\overline{\overline{3,1,2}}) - (\overline{\overline{2,3,1}}) - (\overline{\overline{3,2,1}})]$$

Use of this and eq. (4-3) reduces (5-7) to

$$\frac{\partial e}{\partial t} + \frac{\partial}{\partial x_1}\cdot(eu_1) + \frac{\partial}{\partial x_1}\cdot(\overline{\overline{c_1 \overset{*}{\varepsilon}_{12}}}) - \frac{(N-1)}{2}[(\overline{\overline{1,2}}) - (\overline{\overline{2,1}})]$$

$$- \frac{(N-1)(N-2)}{6}[(\overline{\overline{1,3,2}}) + (\overline{\overline{3,1,2}}) - (\overline{\overline{2,3,1}}) - (\overline{\overline{3,2,1}})] = 0 \qquad (5\text{-}8)$$

Eqn. (5-8) is in the form (5-3), with

$$Q_b = \overline{\overline{c_1 \overset{*}{\varepsilon}_{12}}} - N(N-1)K_a - \frac{N(N-1)(N-2)}{3} K_b \, , \qquad (5\text{-}9)$$

where K_a is the same as before and K_b is given by (4-5), with

$$\phi_b = \int\left(\frac{\partial \varepsilon_{13}}{\partial \xi_1}\cdot F_{12} + \frac{\partial \varepsilon_{13}}{\partial p_1}\cdot G_{12} + \frac{\partial \varepsilon_{13}}{\partial \xi_3}\cdot F_{32} + \frac{\partial \varepsilon_{13}}{\partial p_3}\cdot G_{32}\right) f_{123} \, \frac{dP_1 dP_2 dP_3}{dx_1 dx_2} \qquad (5\text{-}10)$$

The equations of conservation of mass, momentum, angular momentum, and energy are special cases of eqns. (5-5) and (5-8). Since they will be needed later, we shall write them down explicitly.

We adopt the convention that if a quantity has subscript i, it is evaluated at x_i; if there is only one space coordinate involved, we will drop the subscripts.

Mass: $\varepsilon_1 = m$

Eq. (5-5) becomes

$$\frac{\partial\rho}{\partial t} + \frac{\partial}{\partial x}\cdot(\rho u) = 0 \tag{5-11}$$

Momentum: $\varepsilon_1 = m\xi_1$.

Eq. (5-5) becomes

$$\frac{\partial}{\partial t}(\rho u^i) + \frac{\partial}{\partial x^j}(\rho u^i u^j) + \frac{\partial p^{ij}}{\partial x^j} = 0 \ , \tag{5-12}$$

where p^{ij} is the stress tensor and is given by

$$p^{ij} = p^{ij}_{kin} + p^{ij}_{pot}$$

with

$$\begin{aligned} p^{ij}_{kin} &= m\overline{\overline{\xi^i c^j}} \\ &= m\overline{\overline{c^i c^j}} \\ \\ p^{ij}_{pot} &= -N(N-1)K^{ij}_a \end{aligned} \tag{5-13}$$

and

$$\phi^i_a(x_1,x_2) = \int m\, F^i_{12} f_{12} \frac{dP_1 dP_2}{dx_1 dx_2} \ .$$

If the intermolecular forces are central,

$$F^i_{12} = (x^i_2 - x^i_1)F^*(|x_2 - x_1|) \ .$$

where F^* is some function. (Usually, $F^*(|x_2-x_1|) = \frac{1}{r}\frac{d\varepsilon_{12}}{dr}$, where $r = |x_2-x_1|$.)

Let

$$y^i = x_2^i - x_1^i$$

and

$$n_{12}(x_1, x_2) = \int f_{12} \frac{dP_1 dP_2}{dx_1 dx_2} .$$

Then

$$K_a^{ij}(x) = \frac{m}{2} \int y^i y^j F^*(r) \int_o^1 n_{12}(x - \alpha y, x + (1-\alpha)y) \, d\alpha dy . \qquad (5\text{-}14)$$

Angular Momentum

Since, when i, j, k are cyclic, the i-th component of the angular momentum depends on the j-th and k-th components of position and velocity, we will, depending on convenience, denote it with the superscript i or jk.

$$\varepsilon_1^{jk} = m(x_1^j \xi_1^k - x_1^k \xi_1^j) + \mu_1^{jk} ,$$

where μ_1^{jk} is the angular momentum of molecule 1 due to motion relative to its center of mass.

We have

$$\overline{\overline{c_1^i \varepsilon_1^{jk}}} = x_1^j p_{1kin}^{ik} + \overline{\overline{c_1^i \mu_1^{jk}}} - x_1^k p_{1kin}^{ij}$$

$$\frac{\partial \varepsilon_1^{jk}}{\partial \xi_1^{\ell}} F_{12}^{\ell} = m(x_1^j F_{12}^k - x_1^k F_{12}^j) ,$$

and

$$\frac{\partial \varepsilon_1^{jk}}{\partial p_1}\cdot G_{12} = \frac{\partial \mu_1^{jk}}{\partial p_1}\cdot G_{12} .$$

Hence (5-5) takes the form

$$\frac{\partial \overline{\overline{\varepsilon_1^{jk}}}}{\partial t} + \frac{\partial}{\partial x_1^i}(\overline{\overline{\varepsilon_1^{jk}u_1^i}}) + \frac{\partial}{\partial x_1^i}\overline{\overline{c_1^i \varepsilon_1^{jk}}} - N(N-1)\frac{\partial k_1^{ijk}}{\partial x_1^i} = 0 , \qquad (5\text{-}15)$$

where k_1^{ijk} is of the form (4-5), with

$$\phi^{jk} = \int [m(x_1^j F_{12}^k - x_1^k F_{12}^j) + \frac{\partial \mu_1^{jk}}{\partial p_1}\cdot G_{12}] f_{12} \frac{dP_1 dP_2}{dx_1 dx_2} . \qquad (5\text{-}16)$$

Energy $\varepsilon_1 = \frac{1}{2} m \xi_1^2 + \varepsilon_1'''$,

$$e = \overline{\overline{\varepsilon}}_1 + \frac{(N-1)}{2}\overline{\overline{\varepsilon}}_{12} ,$$

where ε_1''' is the kinetic energy of molecule 1 due to motion relative to its center of mass. If the molecules are rigid, such motion reduces to rotation. In that case, if ω^i denotes the angular velocity of a molecule, its internal angular momentum μ^i is given by

$$\mu^i = I^{ij}\omega^j ,$$

where I^{ij} is the inertia tensor of the molecule. Its internal kinetic energy is $\frac{1}{2}I^{ij}\omega^i\omega^j$. In the general case

$$\overline{\overline{c_1^i \varepsilon_1}} = \overline{\overline{c_1^i \varepsilon_1'''}} + \frac{1}{2} m \, \overline{\overline{c_1^2 c_1^i}} + P^{ik}_{1kin} u_1^k \ ,$$

and eqn. (5-8) becomes

$$\frac{\partial e}{\partial t} + \frac{\partial}{\partial x_1} \cdot (e u_1) + \frac{\partial q_1^i}{\partial x_1^i} - N(N-1) \frac{\partial k^i_{1a}}{\partial x_1^i} - \frac{N(N-1)(N-2)}{3} \frac{\partial k^i_{1b}}{\partial x_1^i} = 0 \ , \qquad (5\text{-}17)$$

with

$$q_1^i = \frac{1}{2} m \overline{\overline{c_1^2 c_1^i}} + P^{ik}_{1kin} u_1^k + \overline{\overline{\varepsilon_1''' c_1^i}} + \frac{(N-1)}{2} \overline{\overline{\varepsilon_{12} c_1^i}} \ ,$$

and

$$\phi_a = \int \left(m \xi_1 \cdot F_{12} + \frac{\partial \varepsilon_1'''}{\partial p_1} \cdot G_{12} \right) f_{12} \frac{dP_1 dP_2}{dx_1 dx_2} \ .$$

ϕ_b is given by eqn. (5-10).

6. Conservation Equations for Correlations

We first derive the equation for the joint density of a pair of integrals ε', ε''. Recall that there are three cases:

(1) Both integrals are of type (a).

(2) One integral is of type (a), and the other, of type (b).

(3) Both integrals are of type (b).

Recall also that if

$$Q_{12} = \varepsilon_1'\varepsilon_2'' \qquad \text{in case (1),}$$

$$Q_{12} = \varepsilon_1'\varepsilon_2'' + \frac{(N-2)}{2}\varepsilon_1'\varepsilon_{23}'' \qquad \text{in case (2),}$$

and

$$Q_{12} = \varepsilon_1'\varepsilon_2'' + \frac{(N-2)}{2}(\varepsilon_1'\varepsilon_{23}'' + \varepsilon_2''\varepsilon_{13}') + \frac{(N-2)(N-3)}{4}\varepsilon_{13}'\varepsilon_{24}'' \qquad \text{in case (3),}$$

then, in each case, $\overline{Q}_{12}$ is the joint density (in 3-space) of ε' and ε'' when x_1 and x_2 are far apart.

If one integrates eqn. (2-1) — the Liouville equation — with respect to all but r particles, one gets what is called the r-th equation of the BBGKY hierarchy:

$$\frac{\partial f_{12\ldots r}}{\partial t} + \sum_{i=1}^{r}\left(\frac{\partial f_{12\ldots r}}{\partial x_i}\cdot \xi_i + \frac{\partial f_{12\ldots r}}{\partial q_i}\cdot p_i\right) + \sum_{\substack{i,j=1\\ i\neq j}}^{r}\left(\frac{\partial f_{12\ldots r}}{\partial \xi_i}\cdot F_{ij}\right.$$

$$\left. + \frac{\partial f_{12\ldots r}}{\partial p_i}\cdot G_{ij}\right) + (N-r)\sum_{i=1}^{r}\int\left(\frac{\partial f_{12\ldots r\; r+1}}{\partial \xi_i}\cdot F_{ir+1}\right.$$

$$\left. + \frac{\partial f_{12\ldots r\; r+1}}{\partial p_i}\cdot G_{ir+1}\right) dP_{r+1} = 0 \qquad (6\text{-}1)$$

(It is assumed that the system is isolated.)

Case 1: Multiplying the second BBGKY equation by $N(N-1)Q_{12}$ and integrating with respect to $\frac{dP_1 dP_2}{dx_1 dx_2}$, we get

$$\begin{aligned}
&\frac{\partial\overline{Q}_{12}}{\partial t} + \frac{\partial}{\partial x_1}\cdot(u_1\overline{Q}_{12}) + \frac{\partial}{\partial x_1}\cdot(\overline{c_1Q_{12}}) + \frac{\partial}{\partial x_2}\cdot(u_2\overline{Q}_{12}) + \frac{\partial}{\partial x_2}\cdot(\overline{c_2Q_{12}}) \\
&\quad - \overline{\frac{\partial\varepsilon'_1}{\partial x_1}\cdot\xi_1\varepsilon''_2} - \overline{\frac{\partial\varepsilon'_1}{\partial q_1}\cdot p_1\varepsilon''_2} - \overline{\frac{\partial\varepsilon''_2}{\partial x_2}\cdot\xi_2\varepsilon'_1} - \overline{\frac{\partial\varepsilon''_2}{\partial q_2}\cdot p_2\varepsilon'_1} - \overline{(F_{12}\cdot\frac{\partial\varepsilon'_1}{\partial\xi_1} + G_{12}\cdot\frac{\partial\varepsilon'_1}{\partial p_1})\varepsilon''_2} \\
&\quad - \overline{(F_{21}\cdot\frac{\partial\varepsilon''_2}{\partial\xi_2} + G_{21}\cdot\frac{\partial\varepsilon''_2}{\partial p_2})\varepsilon'_1} - (N-2)[\overline{(F_{13}\cdot\frac{\partial\varepsilon'_1}{\partial\xi_1} + G_{13}\cdot\frac{\partial\varepsilon'_1}{\partial p_1})\varepsilon''_2} \\
&\quad + \overline{(F_{23}\cdot\frac{\partial\varepsilon''_2}{\partial\xi_2} + G_{23}\cdot\frac{\partial\varepsilon''_2}{\partial p_2})\varepsilon'_1}] = 0 \qquad (6\text{-}2)
\end{aligned}$$

If we use eqn. (4-1) and assume that $|x_2 - x_1| > \sigma$, eqn. (6-2) becomes

$$\begin{aligned}
&\frac{\partial\overline{Q}_{12}}{\partial t} + \frac{\partial}{\partial x_1}\cdot(u_1\overline{Q}_{12}) + \frac{\partial}{\partial x_2}(u_2\overline{Q}_{12}) + \frac{\partial}{\partial x_1}\cdot(\overline{c_1Q_{12}}) + \frac{\partial}{\partial x_2}\cdot(\overline{c_2Q_{12}}) \\
&\quad - (N-2)[\overline{(F_{13}\cdot\frac{\partial\varepsilon'_1}{\partial\xi_1} + G_{13}\cdot\frac{\partial\varepsilon'_1}{\partial p_1})\varepsilon''_2} + \overline{(F_{23}\cdot\frac{\partial\varepsilon''_2}{\partial\xi_2} + G_{23}\cdot\frac{\partial\varepsilon''_2}{\partial p_2})\varepsilon'_1}] = 0 \qquad (6\text{-}3)
\end{aligned}$$

The set over which the assumption that $|x_2 - x_1| > \sigma$ fails is a strip of width 2σ in six-dimensional space. But σ is a small parameter, and ultimately we will take a limit in which $\sigma \to 0$. It can be shown by considering the initial value problem that if the terms dropped are small initially, they will remain small over a finite, macroscopic amount of time. Intuitively, this means that if two specific particles are far apart initially, they have a very small probability of coming close to each other within such an amount of time.

Using (4-2) and the formula of Irving and Kirkwood, we can write (6-3) as a conservation equation:

$$\frac{\partial\overline{Q}_{12}}{\partial t} + \frac{\partial}{\partial x_1}\cdot(u_1\overline{Q}_{12}) + \frac{\partial}{\partial x_2}\cdot(u_2\overline{Q}_{12}) + \frac{\partial}{\partial x_1}\cdot(\overline{c_1 Q_{12}}) + \frac{\partial}{\partial x_2}\cdot(\overline{c_2 Q_{12}})$$

$$- N(N-1)(N-2)\left(\frac{\partial}{\partial x_1}\cdot\mathcal{K}^{(1)} + \frac{\partial}{\partial x_2}\cdot\mathcal{K}^{(2)}\right) = 0 \tag{6-4}$$

where

$$\mathcal{K}^{(1)} = \int \varepsilon_2'' K^{(1)}(x_1, P_2)\,\frac{dP_2}{dx_2}$$

with

$$\phi^{(1)}(x_1, x_3) = \int\left(\frac{\partial\varepsilon_1'}{\partial\xi_1}\cdot F_{13} + \frac{\partial\varepsilon_1'}{\partial p_1}\cdot G_{13}\right) f_{123}\,\frac{dP_1 dP_3}{dx_1 dx_3}\ ,$$

and

$$\mathcal{K}^{(2)} = \int \varepsilon_1' K^{(2)}(P_1, x_2)\,\frac{dP_1}{dx_1}$$

with

$$\phi^{(2)}(x_2, x_3) = \int\left(\frac{\partial\varepsilon_2''}{\partial\xi_2}\cdot F_{23} + \frac{\partial\varepsilon_2''}{\partial p_2}\cdot G_{23}\right) f_{123}\,\frac{dP_2 dP_3}{dx_2 dx_3}\ . \tag{6-5}$$

Case 2: On multiplying the third BBGKY equation by $N(N-1)Q_{12}$ and integrating with respect to $\frac{dP_1 dP_2 dP_3}{dx_1 dx_2}$, we get

$$
\begin{aligned}
&\frac{\partial \overline{Q}_{12}}{\partial t} + \frac{\partial}{\partial x_1}\cdot(u_1\overline{Q}_{12}) + \frac{\partial}{\partial x_1}\cdot(\overline{c_1 Q_{12}}) - \overline{(\xi_1\cdot\frac{\partial \varepsilon_1'}{\partial x_1} + p_1\cdot\frac{\partial \varepsilon_1'}{\partial q_1})[\varepsilon_2'' + \frac{(N-2)}{2}\varepsilon_{23}'']} \\
&+ \frac{\partial}{\partial x_2}\cdot(u_2\overline{Q}_{12}) + \frac{\partial}{\partial x_2}\cdot(\overline{c_2 Q_{12}}) - \overline{(\xi_2\cdot\frac{\partial \varepsilon_2''}{\partial x_2} + p_2\cdot\frac{\partial \varepsilon_2''}{\partial q_2})\varepsilon_1'} \\
&- \frac{(N-2)}{2}\overline{(\xi_2\cdot\frac{\partial \varepsilon_{23}''}{\partial x_2} + p_2\cdot\frac{\partial \varepsilon_{23}''}{\partial q_2} + \xi_3\cdot\frac{\partial \varepsilon_{23}''}{\partial x_3} + p_3\cdot\frac{\partial \varepsilon_{23}''}{\partial q_3})\varepsilon_1'} \\
&- \overline{[(F_{12}+F_{13})\cdot\frac{\partial \varepsilon_1'}{\partial \xi_1} + (G_{12}+G_{13})\cdot\frac{\partial \varepsilon_1'}{\partial p_1}][\varepsilon_2'' + \frac{(N-2)}{2}\varepsilon_{23}'']} \\
&- \overline{\varepsilon_1'[(F_{21}+F_{23})\cdot\frac{\partial}{\partial \xi_2} + (G_{21}+G_{23})\cdot\frac{\partial}{\partial p_2}][\varepsilon_2'' + \frac{(N-2)}{2}\varepsilon_{23}'']} \\
&- \frac{(N-2)}{2}\overline{[(F_{31}+F_{32})\cdot\frac{\partial \varepsilon_{23}''}{\partial \xi_3} + (G_{31}+G_{32})\cdot\frac{\partial \varepsilon_{23}''}{\partial p_3}]\varepsilon_1'} \\
&- (N-3)\overline{(F_{14}\cdot\frac{\partial \varepsilon_1'}{\partial \xi_1} + G_{14}\cdot\frac{\partial \varepsilon_1'}{\partial p_1})[\varepsilon_2'' + \frac{(N-2)}{2}\varepsilon_{23}'']} \\
&- (N-3)\overline{(F_{24}\cdot\frac{\partial \varepsilon_2''}{\partial \xi_2} + G_{24}\cdot\frac{\partial \varepsilon_2''}{\partial p_2})\varepsilon_1'} \\
&- \frac{(N-2)(N-3)}{2}\overline{(F_{24}\cdot\frac{\partial \varepsilon_{23}''}{\partial \xi_2} + G_{24}\cdot\frac{\partial \varepsilon_{23}''}{\partial p_2} + F_{34}\cdot\frac{\partial \varepsilon_{23}''}{\partial \xi_3} + G_{34}\cdot\frac{\partial \varepsilon_{23}''}{\partial p_3})\varepsilon_1'} = 0 \quad (6\text{-}6)
\end{aligned}
$$

We observe that the bar denotes integration (with respect to everything except x_1 and x_2) and that, under the integral sign, the dummy indices can be interchanged at will. For example,

$$\overline{F_{24}\cdot\frac{\partial \varepsilon_2''}{\partial \xi_2}\varepsilon_1} = \overline{F_{23}\cdot\frac{\partial \varepsilon_2''}{\partial \xi_2}\varepsilon_1}$$

If this property and the identities (4-1)-(4-3) are used and if $|x_2 - x_1| > 2\sigma$ then eqn. (6-6) becomes

$$\frac{\partial\overline{Q}_{12}}{\partial t}+\frac{\partial}{\partial x_1}\cdot(u_1\overline{Q}_{12})+\frac{\partial}{\partial x_2}\cdot(u_2\overline{Q}_{12})+\frac{\partial}{\partial x_1}\cdot(\overline{c_1Q_{12}})+\frac{\partial}{\partial x_2}\cdot(\overline{c_2Q_{12}})$$

$$-\frac{(N-2)}{2}\overline{\varepsilon_2''(F_{13}\cdot\frac{\partial\varepsilon_1'}{\partial\xi_1}+G_{13}\cdot\frac{\partial\varepsilon_1'}{\partial p_1}-F_{31}\cdot\frac{\partial\varepsilon_3'}{\partial\xi_3}-G_{31}\cdot\frac{\partial\varepsilon_3'}{\partial p_3})}$$

$$-\frac{(N-2)}{2}\overline{(F_{23}\cdot\frac{\partial\varepsilon_2''}{\partial\xi_2}+G_{23}\cdot\frac{\partial\varepsilon_2''}{\partial p_2}-F_{32}\cdot\frac{\partial\varepsilon_3''}{\partial\xi_3}-G_{32}\cdot\frac{\partial\varepsilon_3''}{\partial p_3})\varepsilon_1'}$$

$$-\frac{(N-2)(N-3)}{4}\overline{(F_{14}\cdot\frac{\partial\varepsilon_1'}{\partial\xi_1}+G_{14}\cdot\frac{\partial\varepsilon_1'}{\partial p_1}-F_{41}\cdot\frac{\partial\varepsilon_4'}{\partial\xi_4}-G_{41}\cdot\frac{\partial\varepsilon_4'}{\partial p_4})\varepsilon_{23}''}$$

$$-\frac{(N-2)(N-3)}{2}\overline{(F_{24}\cdot\frac{\partial\varepsilon_{23}''}{\partial\xi_2}+G_{24}\cdot\frac{\partial\varepsilon_{23}''}{\partial p_2}+F_{34}\cdot\frac{\partial\varepsilon_{23}''}{\partial\xi_3}+G_{34}\cdot\frac{\partial\varepsilon_{23}''}{\partial p_3})\varepsilon_1'}=0 \quad (6\text{-}7)$$

Use of (4-4) - (4-6) enables us to write (6-7) as a conservation equation:

$$\frac{\partial\overline{Q}_{12}}{\partial t}+\frac{\partial}{\partial x_1}\cdot(u_1\overline{Q}_{12})+\frac{\partial}{\partial x_2}\cdot(u_2\overline{Q}_{12})+\frac{\partial}{\partial x_1}\cdot(\overline{c_1Q_{12}})+\frac{\partial}{\partial x_2}\cdot(\overline{c_2Q_{12}})$$

$$-N(N-1)(N-2)(\frac{\partial}{\partial x_1}\cdot\mathcal{K}^{(1)}+\frac{\partial}{\partial x_2}\cdot\mathcal{K}^{(2)})$$

$$-\frac{N(N-1)(N-2)}{2}\frac{\partial}{\partial x_1}\cdot\mathcal{K}^{(3)}-\frac{N(N-1)(N-2)(N-3)}{3}\frac{\partial}{\partial x_2}\cdot\mathcal{K}^{(6)}=0, \quad (6\text{-}8)$$

where $\mathcal{K}^{(1)}$ and $\mathcal{K}^{(2)}$ are the same as in (6-5) and

$$\mathcal{K}^{(3)}=\int\varepsilon_{23}''K^{(3)}(x_1,P_2,P_3)\frac{dP_2dP_3}{dx_2},$$

with

$$\phi^{(3)}=\int(\frac{\partial\varepsilon_1'}{\partial\xi_1}\cdot F_{14}+\frac{\partial\varepsilon_1'}{\partial p_1}\cdot G_{14})f_{1234}\frac{dP_1dP_4}{dx_1dx_4},$$

$$\mathcal{K}^{(6)} = \int \varepsilon_1' K^{(6)}(P_1, x_2)\,\frac{dP_1}{dx_1}\,,$$

with

$$\phi^{(6)} = \int \left(\frac{\partial \varepsilon_{23}''}{\partial \xi_2} \cdot F_{24} + \frac{\partial \varepsilon_{23}''}{\partial p_2} \cdot G_{24} + \frac{\partial \varepsilon_{23}''}{\partial \xi_3} \cdot F_{34} + \frac{\partial \varepsilon_{23}''}{\partial p_3} \cdot G_{34} \right) f_{1234}\,\frac{dP_2 dP_3 dP_4}{dx_2 dx_4}$$

Case 3: On multiplying the fourth BBGKY equation by $N(N-1)Q_{12}$ and integrating with respect to $\frac{dP_1 dP_2 dP_3 dP_4}{dx_1 dx_2}$, we get

$$\frac{\partial \overline{Q}_{12}}{\partial t} + \frac{\partial}{\partial x_1} \cdot (u_1 \overline{Q}_{12}) + \frac{\partial}{\partial x_1} \cdot (\overline{c_1 Q_{12}}) + \frac{\partial}{\partial x_2} \cdot (u_2 \overline{Q}_{12}) + \frac{\partial}{\partial x_2} \cdot (\overline{c_2 Q_{12}})$$

$$- \overline{\left(\xi_1 \cdot \frac{\partial \varepsilon_1'}{\partial x_1} + p_1 \cdot \frac{\partial \varepsilon_1'}{\partial q_1}\right) \left[\varepsilon_2'' + \frac{(N-2)}{2} \varepsilon_{23}'' \right]}$$

$$- \overline{\frac{(N-2)}{2} \left(\xi_1 \cdot \frac{\partial \varepsilon_{13}'}{\partial x_1} + p_1 \cdot \frac{\partial \varepsilon_{13}'}{\partial q_1}\right) \left[\varepsilon_2'' + \frac{(N-3)}{2} \varepsilon_{24}'' \right]}$$

$$- \overline{\left(\xi_2 \cdot \frac{\partial \varepsilon_2''}{\partial x_2} + p_2 \cdot \frac{\partial \varepsilon_2''}{\partial q_2}\right) \left[\varepsilon_1' + \frac{(N-2)}{2} \varepsilon_{13}' \right]}$$

$$- \overline{\frac{(N-2)}{2} \left(\xi_2 \cdot \frac{\partial \varepsilon_{24}''}{\partial x_2} + p_2 \cdot \frac{\partial \varepsilon_{24}''}{\partial q_2}\right) \left[\varepsilon_1' + \frac{(N-3)}{2} \varepsilon_{13}' \right]}$$

$$- \overline{\frac{(N-2)}{2} \left(\xi_3 \cdot \frac{\partial \varepsilon_{13}'}{\partial x_3} + p_3 \cdot \frac{\partial \varepsilon_{13}'}{\partial q_3}\right) \left[\varepsilon_2'' + \frac{(N-3)}{2} \varepsilon_{24}'' \right]}$$

$$- \overline{\frac{(N-2)}{2} \left(\xi_4 \cdot \frac{\partial \varepsilon_{24}''}{\partial x_4} + p_4 \cdot \frac{\partial \varepsilon_{24}''}{\partial q_4}\right) \left[\varepsilon_1' + \frac{(N-3)}{2} \varepsilon_{13}' \right]}$$

$$- \overline{\left[\sum_{i=1}^{2} \left(\sum_{\substack{j=1 \\ j \neq i}}^{4} F_{ij} \cdot \frac{\partial}{\partial \xi_i} + G_{ij} \cdot \frac{\partial}{\partial p_i} \right) + (N-4)\left(F_{i5} \cdot \frac{\partial}{\partial \xi_i} + G_{i5} \cdot \frac{\partial}{\partial p_i} \right) \right]}$$

$$\overline{\left[\varepsilon_1' \varepsilon_2'' + \frac{(N-2)}{2} (\varepsilon_1' \varepsilon_{23}'' + \varepsilon_2'' \varepsilon_{13}') + \frac{(N-2)(N-3)}{4} \varepsilon_{13}' \varepsilon_{24}'' \right]}$$

$$
\begin{aligned}
&-\overline{[(F_{31}+F_{32}+F_{34}+(N-4)F_{35})\cdot\frac{\partial}{\partial\xi_3}+(G_{31}+G_{32}+G_{34}+(N-4)G_{35})\cdot\frac{\partial}{\partial p_3}]}\\
&\overline{[\frac{(N-2)}{2}(\varepsilon_1'\varepsilon_{23}''+\varepsilon_2''\varepsilon_{13}')+\frac{(N-2)(N-3)}{4}\varepsilon_{13}'\varepsilon_{24}'']}\\
&-\overline{[(F_{41}+F_{42}+F_{43}+(N-4)F_{45})\cdot\frac{\partial}{\partial\xi_4}+(G_{41}+G_{42}+G_{43}+(N-4)G_{45})\cdot\frac{\partial}{\partial p_4}]}\\
&\overline{[\frac{(N-2)(N-3)}{4}\varepsilon_{13}'\varepsilon_{24}'']}=0 \qquad (6\text{-}9)
\end{aligned}
$$

If, as before, we interchange the dummy indices under the integral sign; use identities (4-1) and (4-3), and assume that $|x_2 - x_1| > 3\sigma$, eqn. (6-9) reduces to

$$
\begin{aligned}
&\frac{\partial\overline{Q}_{12}}{\partial t}+\frac{\partial}{\partial x_1}\cdot(u_1\overline{Q}_{12})+\frac{\partial}{\partial x_2}\cdot(u_2\overline{Q}_{12})+\frac{\partial}{\partial x_1}\cdot(\overline{c_1Q_{12}})+\frac{\partial}{\partial x_2}\cdot(\overline{c_2Q_{12}})\\
&-\frac{(N-2)}{2}\overline{(F_{13}\cdot\frac{\partial\varepsilon_1'}{\partial\xi_1}+G_{13}\cdot\frac{\partial\varepsilon_1'}{\partial p_1}-F_{31}\cdot\frac{\partial\varepsilon_3'}{\partial\xi_3}-G_{31}\cdot\frac{\partial\varepsilon_3'}{\partial p_3})\varepsilon_2''}\\
&-\frac{(N-2)}{2}\overline{(F_{23}\cdot\frac{\partial\varepsilon_2''}{\partial\xi_2}+G_{23}\cdot\frac{\partial\varepsilon_2''}{\partial p_2}-F_{32}\cdot\frac{\partial\varepsilon_3''}{\partial\xi_3}-G_{32}\cdot\frac{\partial\varepsilon_3''}{\partial p_3})\varepsilon_1'}\\
&-\frac{(N-2)(N-3)}{2}\overline{(F_{24}\cdot\frac{\partial\varepsilon_{23}''}{\partial\xi_2}+G_{24}\cdot\frac{\partial\varepsilon_{23}''}{\partial p_2}+F_{34}\cdot\frac{\partial\varepsilon_{23}''}{\partial\xi_3}+G_{34}\cdot\frac{\partial\varepsilon_{23}''}{\partial p_3})\varepsilon_1'}\\
&-\frac{(N-2)(N-3)}{2}\overline{(F_{14}\cdot\frac{\partial\varepsilon_{13}'}{\partial\xi_1}+G_{14}\cdot\frac{\partial\varepsilon_{13}'}{\partial p_1}+F_{34}\cdot\frac{\partial\varepsilon_{13}'}{\partial\xi_3}+G_{34}\cdot\frac{\partial\varepsilon_{13}'}{\partial p_3})\varepsilon_2''}\\
&-\frac{(N-2)(N-3)}{4}\overline{(F_{24}\cdot\frac{\partial\varepsilon_2''}{\partial\xi_2}+G_{24}\cdot\frac{\partial\varepsilon_2''}{\partial p_2}-F_{42}\cdot\frac{\partial\varepsilon_4''}{\partial\xi_4}-G_{42}\cdot\frac{\partial\varepsilon_4''}{\partial p_4})\varepsilon_{13}'}\\
&-\frac{(N-2)(N-3)}{4}\overline{(F_{13}\cdot\frac{\partial\varepsilon_1'}{\partial\xi_1}+G_{13}\cdot\frac{\partial\varepsilon_1'}{\partial p_1}-F_{31}\cdot\frac{\partial\varepsilon_3'}{\partial\xi_3}-G_{31}\cdot\frac{\partial\varepsilon_3'}{\partial p_3})\varepsilon_{24}''}\\
&-\frac{(N-2)(N-3)(N-4)}{4}\overline{(F_{15}\cdot\frac{\partial\varepsilon_{13}'}{\partial\xi_1}+G_{15}\cdot\frac{\partial\varepsilon_{13}'}{\partial p_1}+F_{35}\cdot\frac{\partial\varepsilon_{13}'}{\partial\xi_3}+G_{35}\cdot\frac{\partial\varepsilon_{13}'}{\partial p_3})\varepsilon_{24}''}
\end{aligned}
$$

$$- \frac{(N-2)(N-3)(N-4)}{4}\overline{(F_{25}\cdot\frac{\partial\varepsilon''_{24}}{\partial\xi_2} + G_{25}\cdot\frac{\partial\varepsilon''_{24}}{\partial p_2} + F_{45}\cdot\frac{\partial\varepsilon''_{24}}{\partial\xi_4} + G_{45}\cdot\frac{\partial\varepsilon''_{24}}{\partial p_4})\varepsilon'_{13}}$$

$$= 0 \ . \qquad (6\text{-}10)$$

Use of identity (4-4) and of the Irving-Kirkwood formula enables us to write (6-10) as a conservation equation:

$$\frac{\partial\overline{Q}_{12}}{\partial t} + \frac{\partial}{\partial x_1}\cdot(u_1\overline{Q}_{12}) + \frac{\partial}{\partial x_2}\cdot(u_2\overline{Q}_{12}) + \frac{\partial}{\partial x_1}\cdot(\overline{c_1 Q_{12}}) + \frac{\partial}{\partial x_2}\cdot(\overline{c_2 Q_{12}})$$

$$- N(N-1)(N-2)(\frac{\partial}{\partial x_1}\cdot\mathcal{K}^{(1)} + \frac{\partial}{\partial x_2}\cdot\mathcal{K}^{(2)})$$

$$- \frac{N(N-1)(N-2)(N-3)}{2}(\frac{\partial}{\partial x_1}\cdot\mathcal{K}^{(3)} + \frac{\partial}{\partial x_2}\cdot\mathcal{K}^{(4)})$$

$$- \frac{N(N-1)(N-2)(N-3)}{3}(\frac{\partial}{\partial x_1}\cdot\mathcal{K}^{(5)} + \frac{\partial}{\partial x_2}\cdot\mathcal{K}^{(6)})$$

$$- \frac{N(N-1)(N-2)(N-3)(N-4)}{6}(\frac{\partial}{\partial x_1}\cdot\mathcal{K}^{(7)} + \frac{\partial}{\partial x_2}\cdot\mathcal{K}^{(8)}) = 0 \ , \qquad (6\text{-}11)$$

where $\mathcal{K}^{(1)}$, $\mathcal{K}^{(2)}$, $\mathcal{K}^{(3)}$, and $\mathcal{K}^{(6)}$ are the same as before, and

$$\mathcal{K}^{(4)} = \int \varepsilon'_{13} K^{(4)}(P_1, x_2, P_3)\ \frac{dP_1 dP_3}{dx_1} \ ,$$

with

$$\phi^{(4)} = \int (\frac{\partial\varepsilon''_2}{\partial\xi_2}\cdot F_{24} + \frac{\partial\varepsilon''_2}{\partial p_2}\cdot G_{24}) f_{1234}\ \frac{dP_2 dP_4}{dx_2 dx_4} \ ;$$

$$\mathcal{K}^{(5)} = \int \varepsilon''_2 K^{(5)}(x_1, P_2)\ \frac{dP_2}{dx_2} \ ,$$

with

$$\phi^{(5)} = \int\left(\frac{\partial\varepsilon'_{13}}{\partial\xi_1}\cdot F_{14} + \frac{\partial\varepsilon'_{13}}{\partial p_1}\cdot G_{14} + \frac{\partial\varepsilon'_{13}}{\partial\xi_3}\cdot F_{34} + \frac{\partial\varepsilon'_{13}}{\partial p_3}\cdot G_{34}\right) f_{1234}\,\frac{dP_1dP_3dP_4}{dx_1dx_4} ,$$

$$\mathcal{K}^{(7)} = \int\varepsilon''_{24}K^{(7)}(x_1, P_2, P_4)\frac{dP_2dP_4}{dx_2} ,$$

with

$$\phi^{(7)} = \int\left(\frac{\partial\varepsilon'_{13}}{\partial\xi_1}\cdot F_{15} + \frac{\partial\varepsilon'_{13}}{\partial p_1}\cdot G_{15} + \frac{\partial\varepsilon'_{13}}{\partial\xi_3}\cdot F_{35} + \frac{\partial\varepsilon'_{13}}{\partial p_3}\cdot G_{35}\right) f_{12345}\frac{dP_1dP_3dP_5}{dx_1dx_5} ;$$

and

$$\mathcal{K}^{(8)} = \int\varepsilon'_{13}K^{(8)}(P_1, x_2, P_3)\frac{dP_1dP_3}{dx_1} ,$$

with

$$\phi^{(8)} = \int\left(\frac{\partial\varepsilon''_{24}}{\partial\xi_2}\cdot F_{25} + \frac{\partial\varepsilon''_{24}}{\partial p_2}\cdot G_{25} + \frac{\partial\varepsilon''_{24}}{\partial\xi_4}\cdot F_{45} + \frac{\partial\varepsilon''_{24}}{\partial p_4}\cdot G_{45}\right) f_{12345}\frac{dP_2dP_4dP_5}{dx_2dx_5} .$$

Before we can write down the conservation equations for correlations, we have to introduce some notation:

$$\psi_{12} = f_{12} - f_1f_2 ,$$

$$\psi_{123} = f_{123} - f_1f_2f_3 - [f_1\psi_{23}]^3 ,$$

and

$$\psi_{1234} = f_{1234} - f_1f_2f_3f_4 - [f_1\psi_{234}]^4 - [f_1f_2\psi_{34}]^6 - \alpha[\psi_{12}\psi_{34}]^3 ,$$

where α is some number and where the square brackets indicate a symmetric sum; the number appearing above each sum indicates the number of terms in it. For example,

$$[f_1\psi_{23}]^3 = f_1\psi_{23} + f_2\psi_{13} + f_3\psi_{12} \quad .$$

The above formulas serve as definitions of ψ_{12}, ψ_{123}, etc. In analogy with the definition of the r-particle distribution function, $\psi_{12\ldots r}$ is called the r-particle correlation.

The notation introduced above makes it possible to express the r-particle correlation function in terms of the r-particle distribution function and lower order correlations or, equivalently, lower order distribution functions. Thus if r-particle correlations are ignored, the approximate or truncated r-particle distribution function $\hat{f}_{12\ldots r}$ can be expressed solely in terms of lower order functions. For example,

$$\hat{f}_{123} = f_1f_2f_3 + [f_1\psi_{23}]^3 = -2f_1f_2f_3 + [f_1f_{23}]^3 .$$

The significance of α is that specific values of α give rise to specific ways of defining correlations. For example, $\alpha=1$ gives the well-known Mayer cluster scheme. For more details, see Sec. 7.

If ε', ε'' are any two integrals, we denote the correlation between them by d_{12} and its convective flow by a_{12} and b_{12}. Specifically, in Case (1)

$$d_{12} = \overline{Q}_{12} - \overline{\overline{\varepsilon'_1}}\,\overline{\overline{\varepsilon''_2}} = N(N-1)\int \varepsilon'_1\varepsilon''_2\psi_{12}\frac{dP_1dP_2}{dx_1dx_2} ,$$

$$a_{12} = \overline{c_1Q_{12}} - \overline{\overline{c_1\varepsilon'_1}}\;\overline{\overline{\varepsilon''_2}} = N(N-1)\int c_1\varepsilon'_1\varepsilon''_2\psi_{12}\frac{dP_1dP_2}{dx_1dx_2} ,$$

$$b_{12} = \overline{c_2 Q_{12}} - \overline{\overline{\varepsilon_1'}}\ \overline{\overline{c_2\varepsilon_2''}} = N(N-1)\int c_2\varepsilon_1'\varepsilon_2''\psi_{12}\,\frac{dP_1dP_2}{dx_1dx_2}\ ;$$

in Case (2)

$$d_{12} = \overline{Q}_{12} - \overline{\overline{\varepsilon_1'}}\,\overline{\overline{\varepsilon_2''}} - \frac{(N-2)}{2}\overline{\overline{\varepsilon_1'}}\,\overline{\overline{\varepsilon_{23}''}}$$

$$= N(N-1)\int \varepsilon_1'\varepsilon_2''\psi_{12}\,\frac{dP_1dP_2}{dx_1dx_2}$$

$$+ \frac{N(N-1)(N-2)}{2}\int \varepsilon_1'\varepsilon_{23}''(\psi_{123}+f_2\psi_{13}+f_3\psi_{12})\,\frac{dP_1dP_2dP_3}{dx_1dx_2}\ ,$$

$$a_{12} = N(N-1)\int c_1\varepsilon_1'\varepsilon_2''\psi_{12}\,\frac{dP_1dP_2}{dx_1dx_2}$$

$$+ \frac{N(N-1)(N-2)}{2}\int c_1\varepsilon_1'\varepsilon_{23}''(\psi_{123}+f_2\psi_{13}+f_3\psi_{12})\,\frac{dP_1dP_2dP_3}{dx_1dx_2}\ ,$$

$$b_{12} = N(N-1)\int c_2\varepsilon_1'\varepsilon_2''\psi_{12}\,\frac{dP_1dP_2}{dx_1dx_2}$$

$$+ \frac{N(N-1)(N-2)}{2}\int c_2\varepsilon_1'\varepsilon_{23}''(\psi_{123}+f_2\psi_{13}+f_3\psi_{12})\,\frac{dP_1dP_2dP_3}{dx_1dx_2}\ ;$$

and in Case (3)

$$d_{12} = \overline{Q}_{12} - \overline{\overline{\varepsilon_1'}}\,\overline{\overline{\varepsilon_2''}} - \frac{(N-2)}{2}(\overline{\overline{\varepsilon_1'}}\,\overline{\overline{\varepsilon_{23}''}} + \overline{\overline{\varepsilon_2''}}\,\overline{\overline{\varepsilon_{13}'}}) - \frac{(N-2)(N-3)}{4}\overline{\overline{\varepsilon_{13}'}}\,\overline{\overline{\varepsilon_{24}''}}$$

$$= N(N-1)\int \varepsilon_1'\varepsilon_2''\psi_{12}\,\frac{dP_1dP_2}{dx_1dx_2}$$

$$+ \frac{N(N-1)(N-2)}{2}\int \varepsilon_1'\varepsilon_{23}''(\psi_{123}+f_2\psi_{13}+f_3\psi_{12})\,\frac{dP_1dP_2dP_3}{dx_1dx_2}$$

$$+ \frac{N(N-1)(N-2)}{2}\int \varepsilon_2''\varepsilon_{13}'(\psi_{123}+f_1\psi_{23}+f_3\psi_{12})\,\frac{dP_1dP_2dP_3}{dx_1dx_2}$$

$$+ \frac{N(N-1)(N-2)(N-3)}{4} \int \varepsilon'_{13} \varepsilon''_{24} (\psi_{1234} + [f_1 \psi_{234}]^4 + [f_1 f_2 \psi_{34}]^{4'} + [\psi_{12} \psi_{34}]^{3'})$$

$$\frac{dP_1 dP_2 dP_3 dP_4}{dx_1 dx_2} ,$$

where

$$[f_1 f_2 \psi_{34}]^{4'} = [f_1 f_2 \psi_{34}]^6 - f_1 f_3 \psi_{24} - f_2 f_4 \psi_{13} ,$$

and

$$[\psi_{12} \psi_{34}]^{3'} = \alpha [\psi_{12} \psi_{34}]^3 - \psi_{13} \psi_{24} .$$

a_{12} and b_{12} are defined in the obvious way.

We are now ready to write down the equations for the correlations.

Case (1): Using eqns. (5-5) and (6-4), we get

$$\frac{\partial d_{12}}{\partial t} + \frac{\partial}{\partial x_1} \cdot (u_1 d_{12}) + \frac{\partial}{\partial x_2} \cdot (u_2 d_{12}) + \frac{\partial}{\partial x_1} \cdot a_{12} + \frac{\partial}{\partial x_2} \cdot b_{12} + \frac{\partial}{\partial x_1} \cdot \mathcal{K}^{(1)'}$$

$$+ \frac{\partial}{\partial x_2} \mathcal{K}^{(2)'} = 0 , \qquad (6\text{-}12)$$

where

$$\mathcal{K}^{(1)'} = -N(N-1)(N-2) \mathcal{K}^{(1)} + \bar{\bar{\varepsilon}}''_2 N(N-1) K_{1a} ,$$

and

$$\mathcal{K}^{(2)'} = -N(N-1)(N-2) \mathcal{K}^{(2)} + \bar{\bar{\varepsilon}}'_1 N(N-1) K_{2a}$$

(The K's occuring in eqns. (6-12)- (6-14) are those occuring in eqns. (5-6) and (5-9).)

Case (2): Using eqns. (5-5), (5-8) and (6-8), we get

$$\frac{\partial d_{12}}{\partial t} + \frac{\partial}{\partial x_1}\cdot(u_1 d_{12}) + \frac{\partial}{\partial x_2}\cdot(u_2 d_{12}) + \frac{\partial}{\partial x_1}\cdot a_{12} + \frac{\partial}{\partial x_2}\cdot b_{12} + \frac{\partial}{\partial x_1}\cdot(\mathcal{K}^{(1)'} + \mathcal{K}^{(3)'})$$

$$+ \frac{\partial}{\partial x_2}\cdot(\mathcal{K}^{(2)'} + \mathcal{K}^{(6)'}) = 0 \qquad (6\text{-}13)$$

where $\mathcal{K}^{(1)'}$ and $\mathcal{K}^{(2)'}$ are the same as before, and

$$\mathcal{K}^{(3)'} = -\frac{N(N-1)(N-2)(N-3)}{2}\mathcal{K}^{(3)} + \frac{N(N-1)(N-2)}{2}K_{1a}\overline{\overline{\varepsilon''_{23}}},$$

and

$$\mathcal{K}^{(6)'} = -\frac{N(N-1)(N-2)(N-3)}{3}\mathcal{K}^{(6)} + \frac{N(N-1)(N-2)}{3}K_{2b}\overline{\overline{\varepsilon'_{1}}}.$$

Case (3): Using eqns. (5-8) and (6-11), we get

$$\frac{\partial d_{12}}{\partial t} + \frac{\partial}{\partial x_1}\cdot(u_1 d_{12}) + \frac{\partial}{\partial x_2}\cdot(u_2 d_{12}) + \frac{\partial}{\partial x_1}\cdot a_{12} + \frac{\partial}{\partial x_2}\cdot b_{12}$$

$$(6\text{-}14)$$

$$+ \frac{\partial}{\partial x_1}\cdot(\mathcal{K}^{(1)'} + \mathcal{K}^{(3)'} + \mathcal{K}^{(5)'} + \mathcal{K}^{(7)'}) + \frac{\partial}{\partial x_2}\cdot(\mathcal{K}^{(2)'} + \mathcal{K}^{(4)'} + \mathcal{K}^{(6)'} + \mathcal{K}^{(8)'}) = 0$$

where $\mathcal{K}^{(1)'}$, $\mathcal{K}^{(2)'}$, $\mathcal{K}^{(3)'}$, and $\mathcal{K}^{(6)'}$ are the same as before, and

$$\mathcal{K}^{(4)'} = -\frac{N(N-1)(N-2)(N-3)}{2}\mathcal{K}^{(4)} + \frac{N(N-1)(N-2)}{2}K_{2a}\overline{\overline{\varepsilon'_{13}}},$$

$$\mathcal{K}^{(5)'} = -\frac{N(N-1)(N-2)(N-3)}{3}\mathcal{K}^{(5)} + \overline{\overline{\varepsilon''_{2}}}\,\frac{N(N-1)(N-2)}{3}K_{1b},$$

$$\mathcal{K}^{(7)'} = -\frac{N(N-1)(N-2)(N-3)(N-4)}{6}\mathcal{K}^{(7)} + \frac{(N-3)}{2}\overline{\overline{\varepsilon''_{24}}}\;\frac{N(N-1)(N-2)}{3}K_{1b} ,$$

and

$$\mathcal{K}^{(8)'} = -\frac{N(N-1)(N-2)(N-3)(N-4)}{6}\mathcal{K}^{(8)} + \frac{(N-3)}{2}\overline{\overline{\varepsilon'_{13}}}\;\frac{N(N-1)(N-2)}{3}K_{2b} .$$

Finally, we shall write down the special cases of eqns. (6-12)-(6-14), when the integrals are mass, momentum, angular momentum, or energy.

(1) Mass - Mass

$$\varepsilon'_1 = m, \qquad \varepsilon''_2 = m .$$

$$d_{12} = N(N-1)m^2\int\psi_{12}\,\frac{dP_1dP_2}{dx_1dx_2}$$

$$a^i_{12} = N(N-1)m^2\int c^i_1\psi_{12}\,\frac{dP_1dP_2}{dx_1dx_2}$$

$$b^i_{12} = N(N-1)m^2\int c^i_2\psi_{12}\,\frac{dP_1dP_2}{dx_1dx_2} .$$

$\mathcal{K}^{(1)'i}$ and $\mathcal{K}^{(2)'i}$ vanish. (6-12) becomes

$$\frac{\partial d_{12}}{\partial t} + \frac{\partial}{\partial x^i_1}(u^i_1 d_{12}) + \frac{\partial}{\partial x^i_2}(u^i_2 d_{12}) + \frac{\partial a^i_{12}}{\partial x^i_1} + \frac{\partial b^i_{12}}{\partial x^i_2} = 0 \qquad (6\text{-}15)$$

(2) Mass - Momentum

$$\varepsilon'_1 = m, \qquad \varepsilon''^{j}_2 = m\xi^j_2$$

$$d^j_{12} = N(N-1)m^2\int \xi^j_2 \psi_{12} \frac{dP_1 dP_2}{dx_1 dx_2}$$

$$a^{ij}_{12} = N(N-1)m^2\int c^i_1 \xi^j_2 \psi_{12} \frac{dP_1 dP_2}{dx_1 dx_2} .$$

b^{ij}_{12} is defined similarly.

$$\mathcal{K}^{(1)'ij} = 0 ,$$

and

$$\mathcal{K}^{(2)'ij} = -N(N-1)(N-2)\mathcal{K}^{(2)ij} + \rho_1 N(N-1) K^{ij}_{2a} .$$

$$\mathcal{K}^{(2)ij} = m\int K^{(2)ij}(P_1, x_2) \frac{dP_1}{dx_1} ,$$

with

$$\phi^{(2)j} = m\int F^j_{23} f_{123} \frac{dP_2 dP_3}{dx_2 dx_3} .$$

Let $y^j = x^j_3 - x^j_2$. Then, if the intermolecular forces are central, F^j_{23} depends only on $r = |y|$:

$$F^j_{23} = y^j F^*(r) .$$

Let

$$g_{123}(P_1, x_2, x_3) = \int f_{123} \frac{dP_2 dP_3}{dx_2 dx_3} .$$

Then

$$\phi^{(2)j} = my^j F^*(r) g_{123} \,,$$

and

$$K^{(2)ij} = \frac{m}{2} \int y^i y^j F^*(r) \int_0^1 g_{123}(x_2 - \lambda y, x_2 + (1-\lambda) y) \, d\lambda \, dy \,,$$

where we have suppressed the dependence of g_{123} on P_1.

Recalling that

$$K_{2a}^{ij} = \frac{m}{2} \int y^i y^j F^*(r) \int_0^1 n_{23}(x_2 - \lambda y, x_2 + (1-\lambda) y) \, d\lambda \, dy \,,$$

we obtain

$$\mathcal{K}^{(2)'ij} = - \frac{m^2 N(N-1)(N-2)}{2} \int y^i y^j F^*(r) \int_0^1 (\psi_{123} + f_2 \psi_{13} + f_3 \psi_{12}) \, d\lambda \, dy \, \frac{dP_1}{dx_1} \,,$$

where the integrand of the inner integral has already been integrated with respect to $\frac{dP_2 dP_3}{dx_2 dx_3}$ and is evaluated at $(x_2 - \lambda y, x_2 + (1-\lambda) y)$.

Eq. (6-12) becomes

$$\frac{\partial d_{12}^j}{\partial t} + \frac{\partial}{\partial x_1^i}(u_1^i d_{12}^j) + \frac{\partial}{\partial x_2^i}(u_2^i d_{12}^j) + \frac{\partial a_{12}^{ij}}{\partial x_1^i} + \frac{\partial b_{12}^{ij}}{\partial x_2^i} + \frac{\partial \mathcal{K}^{(2)'ij}}{\partial x_2^i} = 0 \qquad (6\text{-}16)$$

(3) Mass - Angular Momentum

$$\varepsilon_1' = m, \quad \varepsilon_2''^{jk} = m(x_2^j \xi_2^k - x_2^k \xi_2^j) + \mu_2^{jk}$$

$$d_{12}^{jk} = N(N-1) m^2 \int (x_2^j \xi_2^k - x_2^k \xi_2^j) \psi_{12} \frac{dP_1 dP_2}{dx_1 dx_2} + N(N-1) m \int \mu_2^{jk} \psi_{12} \frac{dP_1 dP_2}{dx_1 dx_2} \,.$$

a_{12}^{ijk} and b_{12}^{ijk} are defined in the usual way.

$$\mathcal{K}^{(1)\,'ijk} = 0$$

and

$$\mathcal{K}^{(2)\,'ijk} = -N(N-1)(N-2)\mathcal{K}^{(2)ijk} + N(N-1)\rho_1 K_{2a}^{ijk} .$$

Eq. (6-12) becomes

$$\frac{\partial d_{12}^{jk}}{\partial t} + \frac{\partial}{\partial x_1^i}(u_1^i d_{12}^{jk}) + \frac{\partial}{\partial x_2^i}(u_2^i d_{12}^{jk}) + \frac{\partial a_{12}^{ijk}}{\partial x_1^i} + \frac{\partial b_{12}^{ijk}}{\partial x_2^i} + \frac{\partial \mathcal{K}^{(2)\,'ijk}}{\partial x_2^i} = 0 \qquad (6\text{-}17)$$

(4) Momentum - Momentum

$$\varepsilon_1^{\prime j} = m\xi_1^j , \qquad \varepsilon_2^{\prime\prime K} = m\xi_2^k$$

$$d_{12}^{jk} = N(N-1)m^2 \int \xi_1^j \xi_2^k \psi_{12} \frac{dP_1 dP_2}{dx_1 dx_2} .$$

If the intermolecular forces are central, we proceed in the same way as in the mass - momentum case and obtain

$$\mathcal{K}^{(1)\,'ijk} = -\frac{m^2 N(N-1)(N-2)}{2} \int y^i y^j \xi_2^k F^*(r) \int_0^1 (\psi_{123} + f_1\psi_{23} + f_3\psi_{12})\, d\lambda\, dy \frac{dP_2}{dx_2} ,$$

$$(y^i = x_3^i - x_1^i, \qquad r = |y|)$$

and

$$\mathcal{K}^{(2),ijk} = -\frac{m^2N(N-1)(N-2)}{2}\int y^i y^k \xi_1^j F^*(r)\int_0^1 (\psi_{123}+f_2\psi_{13}+f_3\psi_{12})\,d\lambda\, dy\, \frac{dP_1}{dx_1}$$

$$(y^i = x_3^i - x_2^i, \qquad r = |y|)$$

Eq. (6-12) takes the form

$$\frac{\partial d_{12}^{jk}}{\partial t} + \frac{\partial}{\partial x_1^i}(u_1^i d_{12}^{jk}) + \frac{\partial}{\partial x_2^i}(u_2^i d_{12}^{jk}) + \frac{\partial a_{12}^{ijk}}{\partial x_1^i} + \frac{\partial b_{12}^{ijk}}{\partial x_2^i} + \frac{\partial \mathcal{K}^{(1)'ijk}}{\partial x_1^i} + \frac{\partial \mathcal{K}^{(2)'ijk}}{\partial x_2^i} = 0 \qquad (6\text{-}18)$$

(5) Momentum - Angular Momentum

$$\varepsilon_1'^{j} = m\xi_1^j + \varepsilon_1'''^{j}$$

where $\varepsilon_1'''^{j}$ is the momentum of molecule 1 due to motion relative to its center of mass. Clearly, $\varepsilon_1'''^{j} = 0$ if the molecule is rigid.

$$\varepsilon_2''^{k\ell} = m(x_2^k\xi_2^\ell - x_2^\ell\xi_2^k) + \mu_2^{k\ell} .$$

Defining $d_{12}^{jk\ell}$, $a_{12}^{ijk\ell}$, and $b_{12}^{ijk\ell}$ in the usual way, we see that

$$\frac{\partial d_{12}^{jk\ell}}{\partial t} + \frac{\partial}{\partial x_1^i}(u_1^i d_{12}^{jk\ell}) + \frac{\partial}{\partial x_2^i}(u_2^i d_{12}^{jk\ell}) + \frac{\partial a_{12}^{ijk\ell}}{\partial x_1^i} + \frac{\partial b_{12}^{ijk\ell}}{\partial x_2^i} + \frac{\partial \mathcal{K}^{(2)'ijk\ell}}{\partial x_1^i}$$

$$+ \frac{\partial \mathcal{K}^{(2)'ijk\ell}}{\partial x_2^i} = 0 \qquad (6\text{-}19)$$

(6) Angular Momentum - Angular Momentum

$$\varepsilon_1'^{jk} = m(x_1^j\xi_1^k - x_1^k\xi_1^j) + u_1^{jk} ,$$

$$\varepsilon_2''^{\ell m} = m(x_2^\ell\xi_2^m - x_2^m\xi_2^\ell) + u_2^{\ell m} ,$$

Defining $d_{12}^{jk\ell m}$, $a_{12}^{ijk\ell m}$, and $b_{12}^{ijk\ell m}$ as usual, we get

$$\frac{\partial d_{12}^{jk\ell m}}{\partial t} + \frac{\partial}{\partial x_1^i}(u_1^i d_{12}^{jk\ell m}) + \frac{\partial}{\partial x_2^i}(u_2^i d_{12}^{jk\ell m}) + \frac{\partial a_{12}^{ijk\ell m}}{\partial x_1^i} + \frac{\partial b_{12}^{ijk\ell m}}{\partial x_2^i} + \frac{\partial \mathcal{K}^{(1)'ijk\ell m}}{\partial x_1^i}$$

$$+ \frac{\partial \mathcal{K}^{(2)'ijk\ell m}}{\partial x_2^i} = 0 \tag{6-20}$$

(7) Mass - Energy

$$\varepsilon_1' = m, \qquad \varepsilon_2'' = m\frac{\xi_2^2}{2} + \varepsilon_2'''$$

$$d_{12} = N(N-1)\frac{m^2}{2}\int \xi_2^2 \psi_{12} \frac{dP_1 dP_2}{dx_1 dx_2} + N(N-1)m\int \varepsilon_2''' \psi_{12} \frac{dP_1 dP_2}{dx_1 dx_2}$$

$$+ \frac{N(N-1)(N-2)m}{2}\int \varepsilon_{23}''(\psi_{123} + f_2\psi_{13} + f_3\psi_{12}) \frac{dP_1 dP_2 dP_3}{dx_1 dx_2} .$$

a_{12}^i and b_{12}^i are defined as usual, and

$$\mathcal{J}^{(1)'i} = 0 = \mathcal{K}^{(3)'i} .$$

So, eqn. (6-13) becomes

$$\frac{\partial d_{12}}{\partial t} + \frac{\partial}{\partial x_1^i}(u_1^i d_{12}) + \frac{\partial}{\partial x_1^i}(u_2^i d_{12}) + \frac{\partial a_{12}^i}{\partial x_1^i} + \frac{\partial b_{12}^i}{\partial x_2^i} + \frac{\partial}{\partial x_2^i}(\mathcal{K}^{(2)'i} + \mathcal{K}^{(6)'i}) = 0 \tag{6-21}$$

(8) Momentum - Energy

$$\varepsilon_1'^{\,j} = m\xi_1^j + \varepsilon_1'''^{\,j}$$

$$\varepsilon_2'' = m\,\frac{\xi_2^2}{2} + \varepsilon_2''' \;.$$

We define d_{12}^j, a_{12}^{ij}, and b_{12}^{ij} according to the formula for case (2). Eqn. (6-13) becomes

$$\frac{\partial d_{12}^j}{\partial t} + \frac{\partial}{\partial x_1^i}(u_1^i d_{12}^j) + \frac{\partial}{\partial x_1^i}(u_2^i d_{12}^j) + \frac{\partial a_{12}^{ij}}{\partial x_1^i} + \frac{\partial b_{12}^{ij}}{\partial x_2^i} + \frac{\partial}{\partial x_1^i}(\mathcal{K}^{(1)'ij} + \mathcal{K}^{(3)'ij})$$

$$+ \frac{\partial}{\partial x_2^i}(\mathcal{K}^{(2)'ij} + \mathcal{K}^{(6)'ij}) = 0 \qquad (6\text{-}22)$$

(9) Angular Momentum - Energy

$$\varepsilon_1'^{\,jk} = m(x_1^j\xi_1^k - x_1^k\xi_1^j) + u_1^{jk} \;,$$

$$\varepsilon_2'' = m\,\frac{\xi_2^2}{2} + \varepsilon_2''' \;.$$

The eqn. for the correlation is

$$\frac{\partial d_{12}^{jk}}{\partial t} + \frac{\partial}{\partial x_1^i}(u_1^i d_{12}^{jk}) + \frac{\partial}{\partial x_2^i}(u_2^i d_{12}^{jk}) + \frac{\partial a_{12}^{ijk}}{\partial x_1^i} + \frac{\partial b_{12}^{ijk}}{\partial x_2^i} + \frac{\partial}{\partial x_1^i}(\mathcal{K}^{(1)'ijk} + \mathcal{K}^{(3)'ijk})$$

$$+ \frac{\partial}{\partial x_2^i}(\mathcal{K}^{(2)'ijk} + \mathcal{K}^{(6)'ijk}) = 0 \qquad (6\text{-}23)$$

(10) Energy - Energy

$$\varepsilon_1' = \frac{m\xi_1^2}{2} + \varepsilon_1'''$$

$$\varepsilon_2'' = \frac{m\xi_2^2}{2} + \varepsilon_2''' \ .$$

d_{12}, a_{12}^i, and b_{12}^i are defined according to the formulas for case (3). Eqn. (6-14) looks like

$$\frac{\partial d_{12}}{\partial t} + \frac{\partial}{\partial x_1^i}(u_1^i d_{12}) + \frac{\partial}{\partial x_2^i}(u_2^i d_{12}) + \frac{\partial a_{12}^i}{\partial x_1^i} + \frac{\partial b_{12}^i}{\partial x_1^i} + \frac{\partial}{\partial x_1^i}(\mathcal{K}^{(1)'i} + \mathcal{K}^{(3)'i} + \mathcal{K}^{(5)'i}$$

$$+ \mathcal{K}^{(7)'i}) + \frac{\partial}{\partial x_2^i}(\mathcal{K}^{(2)'i} + \mathcal{K}^{(4)'i} + \mathcal{K}^{(6)'i} + \mathcal{K}^{(8)'i}) = 0 \qquad (6\text{-}24)$$

7. Generalization of the Boltzmann Equation*

The Boltzmann equation, which describes the evolution of f_1 for a rarefied gas, is

$$\frac{\partial f_1}{\partial t} + \xi_1 \cdot \frac{\partial f_1}{\partial x_1} = (N-1) \int (f_{1'} f_{2'} - f_1 f_2) V_{12} d\omega_{12} d\xi_2 \qquad (7\text{-}1)$$

The integral on the right hand side is five-fold and is called the collision integral. Primes denote quantities after collision; the colliding molecules, namely, molecules 1 and 2, are assumed to be at the same point physically. V_{12} is the relative speed (before and after collision) and $d\omega_{12}$ is an element of area in a plane perpendicular to the relative velocity $\xi_2 - \xi_1$.

There exist several derivations of the Boltzmann equation. For quick reference, we shall give below a rough sketch of one of them, which is due to Grad. (For a complete account and a critique, see ref. [1].) All the derivations make two basic assumptions:

(1) Binary Collisions: The only significant collisions are binary collisions, contributions due to higher order collisions being negligible.

(2) Molecular Chaos: Two molecules which are approaching are uncorrelated.

In addition, a limit process is involved and it is assumed that f_1 doesn't vary much over the dimensions of a collision.

Following Grad, we start with the Liouville equation for an isolated system with an intermolecular potential which is central:

---

*The discussion in this section pertains only to rarefied gases.

$$\frac{\partial f}{\partial t} + \sum_{i=1}^{N} \frac{\partial f}{\partial x_i} \cdot \xi_i + \sum_{\substack{i,\,j=1 \\ i \neq j}}^{N} \frac{\partial f}{\partial \xi_i} \cdot F_{ij} = 0 \tag{7-2}$$

Let $\sigma > 0$ be some number, and let $\sim$ denote complements.

For $i \neq r$, let

$$D_r^{(i)} = [P_r: \ |x_r - x_i| > \sigma, \text{ all } \xi_r]$$

and

$$S_r^{(i)} = [x_r: \ |x_r - x_i| = \sigma] \ .$$

Let

$$D = D_2^{(1)} x \ D_3^{(1)} x \ldots x D_N^{(1)} \ ,$$

$$f_1^\sigma(P_1) = \int_D f dP_2 dP_3 \ldots dP_N \ ,$$

and

$$f_{12}^\sigma(P_1, P_2) = \int_{D_3^{(1)} x D_4^{(1)} x \ldots x D_N^{(1)}} f dP_3 \ dP_4 \ldots dP_N$$

f_1^σ gives the probability of finding molecule 1 without any neighbors within a radius of σ. f_{12}^σ, on the other hand, gives the probability of finding molecule 1 with at most one neighbor and is not symmetric in molecules 1 and 2, since the domain of integration depends on 1 but not on 2. Also

$$f_1^\sigma(P_1) = f_1(P_1) - (N-1)\int_{\tilde{D}_2^{(1)}} f_{12}dP_2 + \binom{N-1}{2}\int_{\tilde{D}_2^{(1)}\times\tilde{D}_3^{(1)}} f_{123}dP_2dP_3 - \cdots$$

$$+ (-1)^{N-1}\int_{\tilde{D}_2^{(1)}\times\tilde{D}_3^{(1)}\times\cdots\times\tilde{D}_N^{(1)}} f dP_2dP_3\cdots dP_N$$

and

$$f_{12}^\sigma(P_1,P_2) = f_{12}(P_1,P_2) - (N-2)\int_{\tilde{D}_3^{(1)}} f_{123}dP_3 + \cdots$$

$$+(-1)^{N-2}\int_{\tilde{D}_3^{(1)}\times\tilde{D}_4^{(1)}\times\cdots\times\tilde{D}_N^{(1)}} f dP_3dP_4\cdots dP_N$$

If $N\sigma^3$ is small, f_1^σ and f_{12}^σ approximate f_1 and f_{12} respectively.

In order to derive the equation obeyed by f_1^σ, we will need the following formulas:

$$\int_{|x_2-x_1|>\sigma} \frac{\partial}{\partial x_2}\cdot A(x_1,x_2)dx_2 = -\oint_{|x_2-x_1|=\sigma} A(x_1,x_2)\cdot d\Sigma \quad \text{(Gauss's theorem)} \qquad (7\text{-}3)$$

and

$$\int\limits_{|x_2-x_1|>\sigma} \frac{\partial}{\partial x_1}\cdot A(x_1,x_2)\,dx_2 = \frac{\partial}{\partial x_1}\cdot\int\limits_{|x_2-x_1|>\sigma} A(x_1,x_2)\,dx_2 + \oint\limits_{|x_2-x_1|=\sigma} A(x_1,x_2)\cdot d\Sigma \qquad (7\text{-}4)$$

Now, integration of the Liouville equation over the domain D gives

$$\frac{\partial f_1^\sigma}{\partial t} + \sum_{i=1}^{N} \int_D \frac{\partial f}{\partial x_i}\cdot\xi_i \; dP_2\ldots dP_N + \sum_{\substack{i,j=1\\ i\neq j}} \int_D \frac{\partial f}{\partial \xi_i}\cdot F_{ij} \; dP_2\ldots dP_N = 0$$

Repeated use of (7-4) gives

$$\int_D \frac{\partial f}{\partial x_1}\cdot\xi_1 \; dP_2\ldots dP_N = \frac{\partial}{\partial x_1}\cdot(\xi_1 f_1^\sigma) + (N-1)\int\oint\limits_{S_2^{(1)}} \xi_1 f_{12}^\sigma(P_1,P_2)\cdot d\Sigma_2 \; d\xi_2 \;.$$

Similarly, for $i \geq 2$, use of (7-3) gives

$$\int_D \frac{\partial f}{\partial x_i}\cdot\xi_i \; dP_2\ldots dP_N = -\int\oint\limits_{S_i^{(1)}} \xi_i f_{12}^\sigma(P_1,P_i)\cdot d\Sigma_i \; d\xi_i$$

$$= -\int\oint\limits_{S_2^{(1)}} f_{12}^\sigma(P_1,P_2)\xi_2\cdot d\Sigma_2 \; d\xi_2$$

If, as usual, we assume that the distribution functions vanish at the limits of integration,

$$\sum_{\substack{i,j=1\\ i\neq j}}^{N} \int_D \frac{\partial f}{\partial \xi_i}\cdot F_{ij} \; P_2\ldots dP_N = \sum_{j=2}^{N} \int_D \frac{\partial f}{\partial \xi_i}\cdot F_{ij} dP_2\ldots dP_N$$

$$= (N-1)\int_D \frac{\partial f_{12}^\sigma}{\partial \xi_1}\cdot F_{12} \; dP_1 dP_2 \;.$$

So we finally get

$$\frac{\partial f_1^\sigma}{\partial t} + \xi_1 \cdot \frac{\partial f_1^\sigma}{\partial x_1} + (N-1) \int \oint_{S_2^{(1)}} f_{12}^\sigma(P_1, P_2)(\xi_1 - \xi_2) \cdot d\Sigma_2 \, d\xi_2$$

$$+ (N-1) \int_{D_2^{(1)}} \frac{\partial f_{12}^\sigma}{\partial \xi_1} \cdot F_{12} dP_2 = 0 . \qquad (7\text{-}5)$$

If we now choose σ to be the range of the intermolecular force, the second integral in (7-5) vanishes, since $F_{12}=0$ when $|x_2 - x_1| > \sigma$. So

$$\frac{\partial f_1^\sigma}{\partial t} + \xi_1 \cdot \frac{\partial f_1^\sigma}{\partial x_1} + (N-1) \int \oint_{S_2^{(1)}} f_{12}^\sigma(P_1, P_2)(\xi_1 - \xi_2) \cdot d\Sigma_2 \, d\xi_2 = 0 \qquad (7\text{-}6)$$

This equation already looks a bit like the Boltzmann equation. The resemblance can be made closer by means of a coordinate transformation. Consider the diametral plane of $S_2^{(1)}$ which is perpendicular to the relative velocity $\xi_2 - \xi_1$. Let points in this plane be represented by polar coordinates (r, ε) where $0 \leqq r \leqq \sigma$ and $0 \leqq \varepsilon \leqq 2\pi$. The area element $d\omega_{12}$ in this plane is given by

$$d\omega_{12} = r dr d\varepsilon .$$

Consider the projection of points on $S_2^{(1)}$ onto this plane. The plane is covered twice, but the mapping can be made one-to-one by distinguishing the two hemispheres formed by the plane:

$$S_2^+ : \quad (\xi_2-\xi_1).d\Sigma > 0 \quad \text{(receding particles)}$$

$$S_2^- : \quad (\xi_2-\xi_1).d\Sigma < 0 \quad \text{(approaching particles)}$$

If (r, ε) is a point in the plane, let P_2^+ and P_2^- respectively denote the points on S_2^+ and S_2^- which map into it.

Then equation (7-6) becomes

$$\frac{\partial f_1^\sigma}{\partial t} + \xi_1 \cdot \frac{\partial f_1^\sigma}{\partial x_1} = (N-1)\int [f_{12}^\sigma(P_1, P_2^+) - f_{12}^\sigma(P_1, P_2^-)] V_{12} d\omega_{12} d\xi_2 \tag{7-7}$$

Equation (7-7) can be transformed into (7-1) by performing four steps:

(1) Replace the arguments of $f_{12}^\sigma(P_1, P_2^+, t)$ by the values they must have, say, P_1', P_2', t' at the start of the binary collision in order that they may have the values P_1, P_2^+ at time t. (The start of a collision is defined by $|x_1-x_2| = \sigma$.)

(2) Put

$$f_{12}^\sigma(P_1, P_2^-) = f_1^\sigma(P_1) f_2^\sigma(P_2^-)$$

and

$$f_{12}^\sigma(P_1', P_2', t') = f_1^\sigma(P_1', t') f_2^\sigma(P_2', t') \quad \text{(chaos assumption)}$$

(3) Replace x_1', x_2', x_2^- by x_1 and t_1' by t (slowly varying f).

(4) Replace f_1^σ by f_1 and f_2^σ by f_2 ($N\sigma^3$ small).

It follows that, in order to show that the Boltzmann equation describes a rarefied gas, one has to verify the two basic assumptions made in its derivation. It is intuitively clear, though it hasn't been rigorously proved, that the assumption of binary collisions becomes asymptotically valid as the gas gets more and more rarefied. Concerning the assumption of molecular chaos, however, there seems to be some confusion. As pointed out earlier, it is often stated in the literature that the chaos assumption is also related to the density of the gas; indeed, that it is violated only when the density increases. But we know from the results of the last section that, even for a rarefied gas, there exist situations — such as turbulence — in which correlations are large and persist for macroscopically long times. In order to take such situations into account, we propose the following simple and natural generalization of the Boltzmann equation (actually, of equation (7-7), before making the chaos assumption):

$$\frac{\partial f_1}{\partial t} + \xi_1 \cdot \frac{\partial f_1}{\partial x_1} = (N-1)\int (f_{1'2'} - f_{12}) V_{12} d\omega_{12} d\xi_2 \ ,$$

$$\frac{\partial f_{12}}{\partial t} + \xi_1 \cdot \frac{\partial f_{12}}{\partial x_1} + \xi_2 \cdot \frac{\partial f_{12}}{\partial x_2} + F_{12} \cdot \frac{\partial f_{12}}{\partial \xi_1} + F_{21} \cdot \frac{\partial f_{12}}{\partial \xi_2} = \tag{7-8}$$

$$(N-2)\int (f_{12'3'} - f_{123}) V_{23} d\omega_{23} d\xi_3 + (N-2)\int (f_{1'23'} - f_{123}) V_{13} d\omega_{13} d\xi_3 \ ,$$

and so on. Here, as in the Boltzmann equation, we have assumed that binary collisions are the dominant ones and that the colliding molecules are at the same point physically.

The first two equations of the sequence (7-8) have been postulated and used, together with truncation of f_{123}, for the calculation of transport coefficients by Devanathan and Bhatnagar [16]*.

The sequence (7-8) can be made plausible in a manner similar to Grad's derivation of the Boltzmann equation. Note that the first equation is what the Boltzmann equation would be if the chaos assumption wasn't made. To obtain the second equation, for example, let

$$E_r = D_r^{(1)} \cap D_r^{(2)} \quad (r=3,4,..,N) \ .$$

Let

$$f_{12}^{\sigma\sigma}(P_1, P_2) = \int_{E_3 \times E_4 \times .. \times E_N} f \, dP_3 dP_4 \ldots dP_N \ ,$$

and

$$f_{123}^{\sigma}(P_1, P_2, P_3) = \int_{E_4 \times E_5 \times \ldots \times E_N} f \, dP_4 dP_5 \ldots dP_N \ .$$

$f_{12}^{\sigma\sigma}$ is symmetric in particles 1 and 2; f_{123}^{σ} is invariant under the interchange of 1 and 2 but not of 1 and 3 or of 2 and 3. In other words, f_{123}^{σ} gives the probability that the cluster consisting of molecules 1 and 2 has at most one neighbor. Also

---

* They claim that the equations describe a moderately dense gas. We believe, however, that the dense gas correction is incomplete. The clearest indication of this is the fact that the conservation equations as well as the equilibrium f_{12} they (the sequence (7-8)) lead to are those of a dilute gas.

$$f^{\sigma\sigma}_{12}(P_1,P_2) = f_{12}(P_1,P_2) - (N-2)\int_{\tilde{E}_3} f_{123}dP_3 + \binom{N-2}{2}\int_{\tilde{E}_3 \times \tilde{E}_4} f_{1234}dP_3dP_4 - \ldots$$

$$+ (-1)^{N-2}\int_{\tilde{E}_3 \times \tilde{E}_4 \times \ldots \times \tilde{E}_N} f\, dP_3dP_4\ldots dP_N ,$$

and

$$f^{\sigma}_{123}(P_1,P_2,P_3) = f_{123}(P_1,P_2,P_3) - (N-3)\int_{\tilde{E}_4} f_{1234}dP_4 + \ldots$$

$$+ (-1)^{N-3}\int_{\tilde{E}_4 \times \tilde{E}_5 \times \ldots \times \tilde{E}_N} f\, dP_4dP_5\ldots dP_N .$$

It follows that if $N \rightarrow 0$ and $\sigma \rightarrow 0$ such that $N\sigma^3 \rightarrow 0$ then $f^{\sigma\sigma}_{12}$ and f^{σ}_{123} approach the full distribution functions f_{12} and f_{123} respectively.

Integration of the Liouville equation over $E_3 \times E_4 \times \ldots \times E_N$ and use of the same type of reasoning as in Grad's derivation (except for the chaos assumption) gives the second equation of the sequence (7-8).

A function (of velocity) is called a collisional invariant of a kinetic equation if, on multiplying the collision term of the equation by the function and integrating with respect to the velocity, one gets zero. The word "invariant" is proper, since the operation referred to gives the average change (per unit time) of the function due to collisions. The collisional invariants of the first generalized Boltzmann equation (G.B.E.), i.e. of the first equation of the sequence (7-8), are the same as those of the Boltzmann equation (B.E.), viz., $1, \xi_1^i (i=1,2,3), \xi_1^2$. The proof is the same, too:

Let

$$I = \int (f_{1'2'} - f_{12}) V_{12} d\omega_{12} d\xi_2$$

$$= \int [f_{12}(\xi_1', \xi_2') - f_{12}(\xi_1, \xi_2)] V_{12} d\omega_{12} d\xi_2 \ ,$$

and let ϕ be any function of velocity.

Let

$$I_{\phi_1} = \int \phi(\xi_1)(f_{1'2'} - f_{12}) V_{12} d\omega_{12} d\xi_2 d\xi_1 \ .$$

Interchanging ξ_1 and ξ_2, and therefore ξ_1' and ξ_2', and observing that the Jacobian is 1, $d\omega_{12} = d\omega_{21}$, and $V_{12} = V_{21}$, we get

$$I_{\phi_1} = I_{\phi_2} = \int \phi(\xi_2)(f_{1'2'} - f_{12}) V_{12} d\omega_{12} d\xi_2 d\xi_1$$

Here, we have used the symmetry of f_{12} in the two particles as well as the assumption that the two particles are at the same point. Similarly, interchanging ξ_1 and ξ_1', and ξ_2 and ξ_2', we get

$$I_{\phi_1} = -I_{\phi_1'} = -I_{\phi_2'} \ ,$$

where

$$I_{\phi_1'} = \int \phi(\xi_1')(f_{1'2'} - f_{12})V_{12}d\omega_{12}d\xi_2 d\xi_1 \ ,$$

and similarly for $I_{\phi_2'}$.

So

$$I_{\phi_1} = \frac{1}{4}\int [\phi(\xi_1) + \phi(\xi_2) - \phi(\xi_1') - \phi(\xi_2')][f_{1'2'} - f_{12}]V_{12}d\omega_{12}d\xi_2 d\xi_1 \ . \tag{7-9}$$

Hence

$$I_{\phi_1} = 0$$

if ϕ is a summational invariant, i.e., if

$$\phi(\xi_1) + \phi(\xi_2) = \phi(\xi_1') + \phi(\xi_2') \tag{7-10}$$

By virtue of the laws of conservation of mass, momentum, and energy this is true of $1, \xi_1^i, \xi_1^2$. By a theorem of Grad, any continuous function ϕ satisfying (7-10) is a linear combination of $1, \xi_1^i, \xi_1^2$.

We remark that the reason for the similarity between the above proof and that for the Boltzmann collision term is that f_{12} has the same symmetries as $f_1 f_2$. Also, the same type of reasoning as above shows that the collisional invariants of the second G.B.E. are products of those of the first:

$$\phi_\alpha(\xi_1)\phi_\beta(\xi_2) \ ,$$

where

$$\alpha, \beta = 0,1,2,3,4 ,$$

and

$$\phi_o(\xi_1) = 1, \quad \phi_i(\xi_1) = \xi_1^i \ (i=1,2,3), \ \phi_4(\xi_1) = \xi_1^2 .$$

We have not been able, however, to show that all the collisional invariants are of this form.

The sequence (7-8), like the BBGKY hierarchy, has the property that the equation for* $f^{(r)}$ contains $f^{(r+1)}$ in the collision integrals. In order to solve the sequence, therefore, one should terminate it at some point. If, for example, it is desired to terminate it at the r-th stage, then in the equation for $f^{(r)}$, $f^{(r+1)}$ should be replaced by its truncated form $\hat{f}^{(r+1)}$, which depends only on the lower order distribution functions $f^{(1)}, f^{(2)}, \ldots, f^{(r)}$. Clearly, the truncation cannot be done arbitrarily; certain compatibility criteria should be met. One obvious compatibility condition is

$$\int \hat{f}_{12\ldots r} \, dP_i = f^{(r-1)} = \int f_{12\ldots r} \, dP_i \quad (i=1,2,\ldots,r) \qquad \text{C1}$$

A second condition is that if the truncated r-th G.B.E. is called the r-th B.E., one should have:

Integration of the r-th B.E. with respect to any particle yields the (r-1)-th G.B.E. C2

---

*When the subscripts are unimportant, we shall denote the r-particle distribution function by $f^{(r)}$.

The first condition means simply that the truncated function satisfies the same normalization condition as the untruncated one; in other words, the correlation $f^{(r)} - \hat{f}^{(r)}$ vanishes when integrated with respect to any of the particles. The second condition guarantees that truncation at the r-th stage doesn't imply any loss of information at the lower levels. It may be worth noting that several recent generalizations of the Boltzmann equation [5,17,18,19] satisfy not C2, but the more restrictive condition that the r-th B.E. gives the (r-1)-th B.E. (not G.B.E.) on integration.

There are several ways of truncating the distribution function $f^{(r)}$ subject to conditions C1 and C2, but we shall discuss only three of them in detail. If we impose a third condition, the three truncations turn out to be equivalent in a certain sense.

Consider the moments about the mean of a random variable x.

Let

$$\overline{x} = \int x \, dp ,$$

where dp is some probability measure.

For any positive integer n

$$\int (x - \overline{x})^n dP = \overline{x^n} - n\overline{x^{n-1}}\,\overline{x} + \binom{n}{2}\overline{x^{n-2}}\,\overline{x}^2 - \cdots + (-1)^{n-1}(n-1)\overline{x}^n .$$

Making the association

$$\overline{x} \to f^{(1)} ,$$

$$\int (x - \overline{x})^n \, dp \to \psi^{(n)} \text{ (the n-particle correlation function) ,}$$

and

$$\overline{x^n} \to f^{(n)} ,$$

we obtain a scheme suggested by Grad:

$$f_{12} = f_1 f_2 + \psi_{12}$$

$$f_{123} = f_1 f_2 f_3 + [f_1 \psi_{23}]^3 + \psi_{123}$$

$$f_{1234} = f_1 f_2 f_3 f_4 + [f_1 \psi_{234}]^4 + [f_1 f_2 \psi_{34}]^6 + \psi_{1234} ,$$

and so on. Here, as before, the square brackets indicate sums symmetric in the subscripts, and the number appearing above each sum indicates the number of terms in it.

Similarly, by considering the cumulants of a random variable, one can obtain Mayer's scheme:

$$f_{12} = f_1 f_2 + \mu_{12}$$

$$f_{123} = f_1 f_2 f_3 + [f_1 \mu_{23}]^3 + \mu_{123}$$

$$f_{1234} = f_1 f_2 f_3 f_4 + [f_1 \mu_{234}]^4 + [f_1 f_2 \mu_{34}]^6 + [\mu_{12} \mu_{34}]^3 + \mu_{1234} ,$$

and so on. In general

$$f_{123\ldots r} = f_1 f_2 \cdots f_r + [f_1 \mu_{234\ldots r}] + [f_1 \mu_{23} \mu_{45\ldots r}] + [f_1 \mu_{234} \mu_{56\ldots r}]$$

$$+ \ldots + [f_1 f_2 \mu_{34\ldots r}] + [f_1 f_2 \mu_{34} \mu_{56\ldots r}] + \ldots$$

$$+ [f_1 f_2 \cdots f_{r-2} \mu_{r-1,r}] + [\mu_{12} \mu_{34\ldots r}]$$

$$+ [\mu_{123} \mu_{45\ldots r}] + \text{all distinct products of the}$$

$$\mu^s + \mu_{1234\ldots r} \,.$$

Finally, one can also write

$$f_{12} = f_1 f_2 + \lambda_{12}$$

$$f_{123} = f_1 f_2 f_3 + [f_1 \lambda_{23}]^3 + \lambda_{123}$$

$$f_{1234} = f_1 f_2 f_3 f_4 + [f_1 \lambda_{234}]^4 + [f_{12} \lambda_{34}]^6 + \lambda_{1234} \,,$$

and so on. In general

$$f_{123\ldots r} = f_1 f_2 \cdots f_r + [f_1 \lambda_{234\ldots r}] + [f_{12} \lambda_{34\ldots r}] + [f_{123} \lambda_{45\ldots r}]$$

$$+ \ldots + [f_{1234\ldots r-2} \lambda_{r-1,r}] + \lambda_{12\ldots r} \,.$$

The correlation functions in the three schemes are related to one another as follows:

$$\left.\begin{aligned}
\psi_{12} &= \mu_{12} = \lambda_{12} \\
\psi_{123} &= \mu_{123} = \lambda_{123} \\
\psi_{1234} &= \mu_{1234} + [\mu_{12}\mu_{34}]^3 = \lambda_{1234} + 2[\lambda_{12}\lambda_{34}]^3 \\
\psi_{12345} &= \mu_{12345} + [\mu_{123}\mu_{45}]^{10} = \lambda_{12345} + 2[\lambda_{123}\lambda_{45}]^{10} ,
\end{aligned}\right\} \quad (7\text{-}11)$$

and so on.

The truncated r-particle distribution function is obtained by simply setting the r-particle correlation equal to zero. For example, the truncated four-particle distribution function is given by

$$\hat{f}_{1234} = f_1 f_2 f_3 f_4 + [f_1 \psi_{234}]^4 + [f_1 f_2 \psi_{34}]^6 \qquad \text{(Grad's scheme)}$$

$$\hat{f}_{1234} = f_1 f_2 f_3 f_4 + [f_1 \mu_{234}]^4 + [f_1 f_2 \mu_{34}]^6 + [\mu_{12}\mu_{34}]^3 \quad \text{(Mayer's scheme)}$$

$$\hat{f}_{1234} = f_1 f_2 f_3 f_4 + [f_1 \lambda_{234}]^4 + [f_{12} \lambda_{34}]^6 \qquad \text{(the third scheme}$$

(The truncated one-, two-, three-particle distribution functions are the same in the three schemes, since the correlation functions are the same.)

The three truncations can be combined in one formula:

$$\hat{f}_{1234} = f_1 f_2 f_3 f_4 + [f_1 \psi_{234}]^4 + [f_1 f_2 \psi_{34}]^6 + \alpha[\psi_{12}\psi_{34}]^3 ,$$

where $\alpha=0$ corresponds to Grad's scheme, $\alpha=1$ to Mayer's scheme, and $\alpha=2$ to the third scheme.

Similar formulas for higher order truncations can be given, but they are more complicated. Suffice it to say that the truncated r-particle distribution function is given by

$$\hat{f}_{12\ldots r} = \prod_{i=1}^{r} f_i + [f_1\psi_{23\ldots r}] + \alpha[f_1\psi_{23}\psi_{45\ldots r}] + \beta[f_1\psi_{23}\psi_{45}\psi_{67\ldots r}]$$

$$+ \ldots + \gamma[f_1\psi_{234}\psi_{56\ldots r}] + \ldots + [f_1 f_2\psi_{345\ldots r}]$$

$$+ \delta[f_1 f_2\psi_{34}\psi_{56\ldots r}] + \ldots + [f_1 f_2\cdots f_{r-2}\psi_{r-1,r}]$$

$$+\theta[\psi_{12}\psi_{34\ldots r}] + \text{ all distinct products of the } \psi^{s}.$$

Proper choice of the coefficients $\alpha, \beta\ldots$ gives Grad's scheme, Mayer's scheme, or the third scheme. But if we let them be arbitrary constants subject to C1, we get what may be called the polynomial-type truncation.*

All the truncations mentioned above satisfy C1 and C2. We shall verify this for Grad's scheme, but the proofs are similar in the other cases.

Note that

$$\int f_{12}\, dP_2 = \int f_1 f_2 dP_2 = f_1 ,$$

---

*The Kirkwood superposition hypothesis, which states that

$$\hat{f}_{123} = \frac{f_{12}f_{23}f_{13}}{f_1 f_2 f_3} ,$$

and its generalization [20] constitute a different type of truncation. In the limit of small two-particle correlations, the Kirkwood hypothesis coincides with the three types discussed here. No such relation seems to exist between its generalization and the three schemes in the higher orders.

i.e.,

$$\int \psi_{12} dP_2 = 0 \ .$$

By symmetry,

$$\int \psi_{12} dP_1 = 0 \ .$$

Using this, one can show that ψ_{123} gives zero when integrated with respect to any of the particles. For the general case, let $\psi^{(2)}$, $\psi^{(3)}$, ... , $\psi^{(r-1)}$ have this property. Then if

$$\hat{f}_{12\ldots r} = \prod_{i=1}^{r} f_i + [f_1 \psi_{23\ldots r}]^r + [f_1 f_2 \psi_{34\ldots r}]^{\binom{r}{2}} + \ldots$$
$$+ [f_1 f_2 \cdots f_{r-2} \psi_{r-1,r}]^{\binom{r}{2}}$$

is integrated with respect to any particle, say the r-th one, the only terms in the symmetric sums which give non-zero contributions are those in which the subscript r is not associated with the correlation functions. One gets

$$\prod_{i=1}^{r-1} f_i + \psi_{12\ldots r-1} + [f_1 \psi_{23\ldots r-1}]^{r-1} + [f_1 f_2 \psi_{34\ldots r-1}]^{\binom{r-1}{2}} + \ldots$$
$$+ [f_1 f_2 \cdots f_{r-3} \psi_{r-2,r-1}]^{\binom{r-1}{2}} ,$$

which equals $f_{12\ldots r-1}$.

We observe that the r-th G.B.E., when it is integrated with respect to a particle, gives the (r-1)-th G.B.E. To show this, one has to use the same argument as is employed to find the collisional invariants and, in addition, assume either that the force terms on the left-hand side of the r-th G.B.E., which contribute on integration to the collision terms of the (r-1)-th G.B.E., can be put (after integration) in the form of the collision terms of the G.B.E.'s, or that those terms can be ignored in comparison with the collision terms of the (r-1)-th G.B.E. and that $N-r \simeq N-r+1$.

To show that Grad's scheme satisfies C2 it is sufficient to consider the collision terms. First consider the second B.E. The collision terms are

$$(N-2)\int(\hat{f}_{12'3'}-\hat{f}_{123})V_{23}d\omega_{23}d\xi_3 \text{ and } (N-2)\int(\hat{f}_{1'23'} - \hat{f}_{123})V_{13}d\omega_{13}d\xi_3 .$$

Let us integrate with respect to particle 2. In the second integral 2 is just a parameter, and so the order of integration can be reversed. By C1, we get $(N-2)\int(f_{1'3'} - f_{13})V_{13}d\omega_{13}d\xi_3$, which, except for the multiplicative factor, is the collision term of the first G.B.E. It remains to show that the other integral gives zero.

Note that

$$\hat{f}_{123} = -2f_1f_2f_3 + [f_1f_{23}]^3 .$$

So we get

$$\int(\hat{f}_{12'3'} - \hat{f}_{123}) V_{23} d\omega_{23} d\xi_3 dP_2 = -2f_1 \int(f_{2'}f_{3'} - f_2 f_3) V_{23} d\omega_{23} d\xi_3 dP_2$$

$$+ f_1 \int(f_{2'3'} - f_{23}) V_{23} d\omega_{23} d\xi_3 dP_2$$

$$+ \int(f_{2'}f_{13'} + f_{3'}f_{12'} - f_2 f_{13} - f_3 f_{12}) V_{23} d\omega_{23} d\xi_3 dP_2 \ .$$

It follows from the same argument as is used to find the collisional invariants that each of the three integrals on the right hand side of the above equation vanishes. The reason why the argument works is that the integrand in each case is symmetric in the colliding particles.

It is clear from the above discussion that any truncation which retains the symmetry in the particles and satisfies C1 satisfies C2. This is true of all the truncations we have discussed, in particular that of Grad in which

$$\hat{f}_{12\ldots r} = (-1)^r (r-1) \prod_{i=1}^{r} f_i + \sum_{j=1}^{r-2} (-1)^{j+1} [f_1 f_2 \cdots f_j f_{j+1\ldots r}]^{\binom{r}{j}} \ .$$

Finally we come to the third condition, which we have referred to earlier. The question we are interested in is whether chaos is propagated in time. In other words, if the long-range correlation is zero initially, will it remain zero for a macroscopically long time? (If so, it implies that the r-th B.E. together with the initial condition gives the (r-1)-th B.E. on integration.) The answer would be in the affirmative if one could prove an existence and uniqueness theorem for the correlation equation and if the equation was homogeneous in the correlation. We shall show that, under certain additional assumptions, the condition of homogeneity is satisfied by all the three truncations we have discussed. Moreover, the correlation equation is the same for the three truncations, and it is in this sense that they are all equivalent. (Strictly speaking, the correlation equations are not the same in the three cases, but each of them can be obtained from either of the other two by using the equations for lower order correlations.)

Recall that the sequence (7-8) is valid when $\varepsilon = N\sigma^3 << 1$. If the Mach number M of the flow is small, one can assume that there is a parameter δ independent of ε, but depending on M such that the correlations are ordered in powers of δ:

$$\begin{aligned} f^{(1)} &\sim 1 \\ \psi^{(2)} &\sim \delta^2 \\ \psi^{(3)} &\sim \delta^3 \\ \psi^{(4)} &\sim \delta^4 , \end{aligned} \tag{7-12}$$

and so on. It follows from (7-11) that if the ψ^s are ordered according to (7-12), so are the μ^s and the λ^s.

The existence of statistical fluctuations implies [21] that δ can't be smaller than ε but that δ can be $>>\varepsilon$. So, if we restrict ourselves to those situations in which

$$\varepsilon << \delta << 1 ,$$

we can use the sequence (7-8) with the ordering for the correlations. Also, for the purpose of studying long-range correlations, one can ignore the force terms on the left hand side of the equations, since it is reasonable to assume that any two specific molecules which are far apart initially have a very small probability of colliding with each other after a finite amount of time. (The second equation of (7-8) with the force terms ignored gives the macroscopic correlation equations (6-12), but without the potential parts of the flow.)

As an example, consider the equation for ψ_{123}. In writing it down, we shall put $N-1 \simeq N-2 \simeq N-3$. Simple substitution and use of the first three equations of the sequence (7-8) gives

$$\frac{\partial\psi_{123}}{\partial t} + \sum_{i=1}^{3} \xi_i \cdot \frac{\partial\psi_{123}}{\partial x_i} + \sum_{\substack{i,j=1 \\ i\neq j}}^{3} \frac{\partial\psi_{123}}{\partial\xi_i} \cdot F_{ij} + \frac{1}{2}\sum_{\substack{i,j,k=1 \\ i\neq j\neq k}}^{3} [\frac{\partial f_i}{\partial\xi_i} \cdot (F_{ij} + F_{ik})\psi_{jk}$$

$$+ f_i(F_{ji} \cdot \frac{\partial\psi_{jk}}{\partial\xi_j} + F_{ki} \cdot \frac{\partial\psi_{jk}}{\partial\xi_k})] = \{f_{\underline{1}}\psi_{23\underline{x}} + f_{\underline{x}}\psi_{\underline{1}23} + (1 \leftrightarrow 2,3)\}$$

$$+ \{\alpha[\psi_{\underline{1}2}\psi_{3\underline{x}}]^3 + (1 \leftrightarrow 2,3)\} - \{[\psi_{\underline{1x}}\psi_{23}]^3\} + \{\psi_{\underline{1}23\underline{x}} + (1 \leftrightarrow 2,3)\}$$

Here, the brackets { } mean that what is enclosed is a collision term; the underlined subscripts refer to colliding particles. The subscript x stands for the particle with which each of 1, 2, and 3 collides. The symbol $(1 \leftrightarrow 2,3)$ means similar terms are to be added with 1 replaced by 2 and 3. If now we ignore the force terms and use the ordering, we get

$$\frac{\partial \psi_{123}}{\partial t} + \sum_{i=1}^{3} \xi_i \cdot \frac{\partial \psi_{123}}{\partial x_i} = \{ f_{\underline{1}} \psi_{23\underline{x}} + f_{\underline{x}} \psi_{\underline{1}23} + (1 \leftrightarrow 2,3) \} \ ,$$

ignoring terms of order δ^4.

Similarly, in the general case

$$\frac{\partial \psi_{123\ldots r}}{\partial t} + \sum_{i=1}^{r} \xi_i \cdot \frac{\partial \psi_{123\ldots r}}{\partial x_i} = \{ f_{\underline{1}} \psi_{23\ldots r\underline{x}} + f_{\underline{x}} \psi_{\underline{1}23\ldots r} + (1 \leftrightarrow 2,3,\ldots r)$$

ignoring terms of order δ^{r+1}.

8. Concluding Remarks

We have shown that, except in a small part of the configuration space, long-range macroscopic correlations in a fluid are conserved. Since the derivation does not depend on the density of the fluid, the equations of conservation are valid for a liquid as well as a gas. Zhigulev and, independently, Tsugé obtained these equations for a rarefied gas, and our equations agree with theirs when the terms containing the intermolecular potential or force explicitly are ignored. Their work as well as ours shows that contrary to the pessimism expressed by certain authors — Monin [22], for example — there is reason to hope that a full-fledged kinetic theory of turbulence can be formulated. The next step toward that end is to study the properties of eqns. (6-12)-(6-14) and to try to solve them. For a rarefied gas, Tsugé has already done some of this work by using the two-point version of the 13-moment method. Finally, the results of Section 7 show that two-point, three-point, etc. kinetic equations for a rarefied gas can be obtained by generalizing the Boltzmann equation in a manner made unique in a certain sense by the imposition of certain compatibility criteria.

References

1. H. Grad, "Principles of the Kinetic Theory of Gases" in Handbuch der Physik, edited by S. Flugge (Springer Verlag, Berlin, 1958), vol. XII.
2. M.N. Kogan, "Rarefied Gas Dynamics", Plenum Press, New York, 1969.
3. H. Grad, "Singular Limits of Solutions of Boltzmann's Equation", NYU-Courant Institute of Mathematical Sciences Report, MF-77, 1972; to appear in the Proceedings of the Eighth International Symposium on Rarefied Gas Dynamics, held at Stanford University in July 1972.
4. L.D. Landau and E.M. Lifshitz, "Fluid Mechanics", Pergamon Press, 1959.
5. R.F. Fox and G.E. Uhlenbeck, Phys. Fluids 13, 2881 (1970).
6. V.N. Zhigulev, Soviet Phys. Doklady 10, 1003 (1966). (Russian original: Doklady Akademii Nauk SSSR 165, 502 (1965).)
7. S. Tsugé, Phys. Letters 33A, 145 (1970).
8. S. Tsugé, "The Boltzmann and Klimontovich Formalisms with reference to Turbulence Resolution", to appear in the Proceedings of the Eighth International Symposium on Rarefied Gas Dynamics, held at Stanford University in July 1972.
9. S.K. Srinivasan, "A New Approach to the Kinetic Theory of Fluids-Onset of Turbulent Motion" in Symposia on Theoretical Physics and Mathematics, edited by A. Ramakrishnan (Plenum Press, New York, 1968), vol. 7; also see references cited therein.
10. H. Grad, Comm. Pure and Appl. Math. 5, 455 (1952).

11. H. Grad, J. Phys. Chem. 56, 1039 (1952).

12. R.M. Lewis, Arch. Ratl. Mech. Anal. 5, 355 (1960).

13. J.S. Dahler, J. Chem. Phys. 30, 1447 (1959).

14. A.C. Eringen, Intl. J. Engineering Science 2, 205 (1964).

15. J.H. Irving and J.G. Kirkwood, J. Chem. Phys. 18, No. 6 (1950).

16. C. Devanathan and P.L. Bhatnagar, Proc. Roy. Soc. A 309, 245 (1969).

17. B.B. Saleeby and M.B. Lewis, Phys. Fluids 14, 1931 (1971).

18. D. Montgomery, Phys. Fluids 12, 804 (1969).

19. F.L. Hinton, Phys. Fluids 13, 857 (1970).

20. G.V. Ramanathan, J.M. Dawson, and M.D. Kruskal, J. Math. Phys. 11, 339 (1970).

21. H. Grad, J. Chem. Phys. 33, 1342 (1960).

22. A.S. Monin, PMM J. Appl. Math. and Mech. (translated from the Russian) 31, No. 6, 1057 (1967).

Official Addressees

Chief Scientist
AF Avionics Laboratory
Wright-Patterson AFB, OH 45433

Chief Scientist
AF Aero Propulsion Laboratory
Wright-Patterson AFB, OH 45433

Chief Scientist
AF Armament Laboratory
Eglin AFB, FL 32542

Chief Scientist
AF Cambridge Research Laboratories
L G Hanscom Fld, Bedford, MA 01730

Chief Scientist
AF Flight Dynamics Laboratory
Wright-Patterson AFB, OH 45433

Chief Scientist
AF Human Resources Laboratory
Brooks AFB, TX 78735

Chief Scientist
AF Materials Laboratory
Wright-Patterson AFB, OH 45433

AF Office of Scientific Research/NM (16 copies)
Attn: Dr. R. G. Pohrer
1400 Wilson Blvd, Arlington, VA 22209

Chief Scientist
AF Rocket Propulsion Laboratory
Edwards AFB, CA 93523

Chief Scientist
AF Weapons Laboratory
Kirtland AFB, NM 87117

Chief Scientist
Aerospace Research Laboratories
Wright-Patterson AFB, OH 45433

Chief Scientist
Frank J. Seiler Research Laboratory
USAF Academy, CO 80840

Chief Scientist
Rome Air Development Center
Griffiss AFB, NY 13440

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)*
New York University
Magneto-Fluid Dynamics Division
251 Mercer St., New York, N.Y. 10012

2a. REPORT SECURITY CLASSIFICATION
UNCLASSIFIED

2b. GROUP

3. REPORT TITLE
LONG-RANGE CORRELATIONS IN KINETIC THEORY

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*
Scientific Interim

5. AUTHOR(S) *(First name, middle initial, last name)*
Chelluri C. A. Sastri

6. REPORT DATE
October 1973

7a. TOTAL NO. OF PAGES
74

7b. NO. OF REFS
22

8a. CONTRACT OR GRANT NO.
AFOSR-71-2053

b. PROJECT NO.
9749-01

c. 61102F
681304

d.

9a. ORIGINATOR'S REPORT NUMBER(S)

9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*
AFOSR-TR-73-1238

10. DISTRIBUTION STATEMENT
1. This document has been approved for public release and sale; its distribution is unlimited.

11. SUPPLEMENTARY NOTES
TECH OTHER

12. SPONSORING MILITARY ACTIVITY
Air Force Office of Scientific Res.
1400 Wilson Boulevard (SRMA)
Arlington, Virginia 22209

13. ABSTRACT

It is shown that macroscopic correlations in a fluid are conserved for macroscopically long times. The equations of conservation can be written in a form independent of the density of the fluid and are therefore valid for a liquid as well as a gas. For the purpose of describing correlations in a rarefied gas, a generalization of the Boltzmann equation is suggested which not only gives the correct macroscopic correlation equations but satisfies certain compatibility criteria.

DD FORM 1 NOV 65 1473

Security Classification

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT

SEP 10 1973

DATE DUE

GAYLORD			PRINTED IN U.S.A.